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EDITED BY

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AMERICAN

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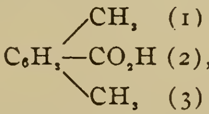
Contributions from the Chemical Laboratory of Rose Polytechnic Institute.

XV.—CAMPHORIC ACID.

SIXTH PAPER.

By William A. Noyes.

Reduction of the Neighboring Xylic Acid.

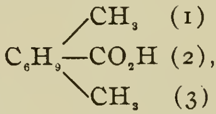
The methods finally used for the synthesis of the neighboring xylic acid  $C_6H_3\begin{matrix}CH_3\ (1)\\ CO_2H\ (2)\\ CH_3\ (3)\end{matrix}$, have already been given.[1]

The acid was reduced by amyl alcohol and sodium. The acid was dissolved in four or five times its weight of amyl alcohol in a flask connected with an upright condenser. The solution was heated to boiling and sodium was dropped in, in portions, from the top of the condenser, the total amount used being twice the weight of the acid. More amyl alcohol was also dropped in through the condenser at such a rate as to keep up a moderately vigorous action and prevent the formation of crusts on the sodium or on the bottom of the flask. When the sodium was dissolved, the contents of the flask was allowed to cool slightly, a small amount of water was added, and the amyl alcohol was distilled off with a current of steam. The alkaline solution was cooled, acidified with sulphuric acid, and extracted twice with ether. The acid obtained by each extraction was dried separately, after distilling away the ether, by heating on the water-bath, reducing the pressure to 30 mm. or less, and shaking vigorously for some minutes. The two portions are dried separately, since the ethereal solution containing the main portion of the acid, takes up much less water than the second, dilute solution. This method of treatment has been found, in many cases, a very quick and satisfactory means of drying substances with boiling-points above 200°.

---

[1] This Journal, **20**, 789.

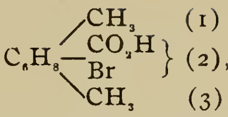
The residual acid was reduced a second and a third time in the same manner. After the third reduction the alkaline solution was acidified with sulphuric acid, sodium carbonate was added to alkaline reaction, the solution thoroughly cooled, and potassium permanganate added till the pink color was permanent for some minutes. This destroys unsaturated acids which are always present. Some acid sodium sulphite was then added and sulphuric acid, more of the sulphite being used to just dissolve the oxides of manganese in the acid solution. The hexahydro acid was then distilled with steam. Unless too much isovaleric acid has been formed, the acid separates in solid form from the distillate, and after filtering off, washing and drying, it is practically pure. A small additional amount, contaminated with isovaleric acid, from which it can be easily separated, may be obtained by extracting the filtrate. A yield of about 50 per cent was obtained.



Hexahydroxylic Acid, $C_6H_9\begin{cases} CH_3 & (1) \\ CO_2H & (2) \\ CH_3 & (3) \end{cases}$, may be purified by crystallization from ligroin or benzene, in both of which it is very easily soluble. It melts at 72° and boils at 250°-252°. The xylic acid boils at 274°.5.

0.1227 gram of the acid gave 0.1136 gram H_2O, and 0.3117 gram CO_2.

	Calculated for $C_9H_{16}O$.		Found.
C_9	108	69.87	69.28
H_{16}	16	10.22	10.29
O_2	32	....	....
	156		



α-Bromhexahydroxylic Acid, $C_6H_8\begin{cases}CH_3 & (1)\\ \left.\begin{matrix}CO_2H\\ Br\end{matrix}\right\} & (2)\\ CH_3 & (3)\end{cases}$, was prepared by treating the hexahydro acid with phosphorus pentachloride and bromine.[1] The chloride of the brom acid, prepared in this way, is quite stable toward water, and may even be heated on the water-bath for some time, with a 10 per cent solution of sodium hydroxide, without passing into solution. It is readily decomposed, however, on warming for twenty or thirty minutes with two or three times its weight of glacial formic acid. The acid crystallizes from formic acid, in which it is rather difficultly soluble, in leaflets which melt at 150°-151°. The acid dissolves in a cold solution of sodium hydroxide without decomposition, but on warming the solution it is decomposed, chiefly with the formation of the tetrahydro acid.

0.1076 gram of the acid gave 0.0860 gram AgBr.

	Calculated for $C_9H_{15}BrO_2$.	Found.
Br	34.04	34.01

Δ^1-Tetrahydroxylic Acid.—When the α-brom acid is warmed with alcoholic potash it loses hydrobromic acid and passes over into the Δ^1-tetrahydroxylic acid. This acid is difficultly soluble in water, easily soluble in alcohol and ether. It is much less easily soluble in ligroin than the hexahydro acid but is more easily soluble than the neighboring xylic acid. It separates, on cooling the solution in warm ligroin, in compact crystals which melt at 89°-90°. The conduct of the acid towards potassium permanganate is remarkable. A solution of the acid in sodium carbonate decolorizes that reagent only very slowly and it was at first thought, on that account, that the acid was the hydroxy acid. The analysis, however, left no doubt as to its composition.

0.1473 gram of the acid gave 0.1209 gram H_2O, and 0.3791 gram CO_2.

	Calculated for $C_9H_{14}O_2$.		Found.
C_9	108	70.13	70.19
H_{14}	14	9.09	9.12
O_2	32	....	....
	154		

---

[1] Baeyer: Ann. Chem. (Liebig), **245**, 175; Aschan: *Ibid.*, **271**, 265.

The properties of the tetrahydroxylic acid, hexahydroxylic acid, and α-bromhexahydroxylic acid leave no possible doubt as to their non-identity with cis-campholytic[1] acid and its derivatives.

Tetrahydroxylic acid melts at 89°-90°, while cis-campholytic acid melts at 133°. The structure of the tetrahydroxylic acid is such that it is highly improbable that the cis-campholytic acid should be a stereomeric modification of the tetrahydroxylic acid.[2] Hexahydroxylic acid melts at 72° and boils at 250°-252°. Dihydrociscampholytic acid is a liquid which boils at 245°-246°. Hexahydroxylic acid is heavier than water and sinks in it. Dihydrociscampholytic acid has the specific gravity 0.9833 at 20°.

The demonstration here furnished of the non-identity of tetrahydroxylic acid and cis-campholytic acid excludes Collie's formula for camphoric acid[3] from further consideration as a possible expression for its structure.

Since this work was undertaken, the synthesis of camphoronic acid by W. H. Perkin, Jr., has furnished a practically complete demonstration that camphoric acid is a derivative of cyclopentane. The low boiling-point and low specific gravity of dihydrociscampholytic acid point strongly in the same direction.

Esterification experiments with the neighboring xylic acid and its hexahydro and tetrahydro derivatives have given results of some interest in their bearing on the constitution of benzene. An account of these is reserved for a later communication.

---

[1] I retain here the nomenclature which I suggested some time ago, though it has not yet been generally accepted. As was first shown by myself (This JOURNAL, **16**, 501; **17**, 428, 433; **18**, 686; Ber. d. chem. Ges., **28**, 547, 553; **29**, 2326), Walker's campholytic acid and Koenig's and Hoerlin's isolauronolic acid both retain the secondary carboxyl of camphoric acid, and this corresponds to the methylene group of camphor; while Fittig and Woringer's lauronolic acid and Walker's allocampholytic acid (called by myself, almost simultaneously, γ-lauronolic acid) retain the tertiary carboxyl of camphoric acid, corresponding to the carbonyl of camphor. W. H. Perkin, Jr., has very recently (Jour. Chem. Soc. (London), **73**, 815) given a clear statement of a part of these relations and they seem to be thoroughly established. It seems very desirable that these relations should be expressed in the nomenclature and that the two acids with secondary carboxyl should be called campholytic and iso-campholytic (or cis-campholytic), and the two with tertiary carboxyl, lauronolic and iso-lauronolic (or γ-lauronolic). A little temporary confusion appears to the writer better than a perpetuation of the present misleading nomenclature.

[2] For a discussion of a somewhat similar case see this JOURNAL, **18**, 690.

[3] Ber. d. chem. Ges., **25**, 1116.

Mr. J. W. Shepherd, working in this laboratory, has succeeded in obtaining a small amount of the α-hydroxydihydrociscampholytic acid. This, by distillation with lead peroxide and dilute sulphuric acid, has given a ketone, presumably the same as that obtained by Mr. Harris.[1] The study of this ketone has proved to be of more than usual interest and we hope to report upon the matter in the near future.

TERRE HAUTE, April 4, 1899.

CONTRIBUTION TO OUR KNOWLEDGE OF AQUEOUS SOLUTIONS OF DOUBLE SALTS.

II.—CHLORIDES.

BY HARRY C. JONES AND KENJIRO OTA.

The condition of a number of double sulphates in solution in water, has already been studied by Jones and Mackay.[2] They determined the conductivity and freezing-point lowering of the constituent sulphates, then the conductivity and freezing-point lowering of the double sulphate at the same dilution, and by comparing these values, were able to draw conclusions as to the condition of the double salt in the solution.

They found for a number of the alums, that the conductivity and freezing-point lowering of the double salt were less than the sum of these values for the constituents, in the more concentrated solutions. But as the dilution increased the difference became smaller, and at great dilution practically disappeared. They concluded from their measurements of conductivity, upon which, in this case, the greater stress is to be laid, that the complex alum molecules are completely broken down in dilute solution, into the molecules of the simpler sulphates, and that these simpler molecules dissociate as if alone, barring the effect produced on the dissociation when the solutions are not isohydric. But that in concentrated solutions, the difference being much greater than that found in the case of mixtures of sulphates incapable of yielding a double salt, pointed to the conclusion that the alums are partially undecomposed into the constituent molecules in such solutions. The freezing-point determinations pointed to the same conclusion, that the alum molecules exist to some extent in the more concentrated solutions.

---

[1] This JOURNAL, **18**, 694.

[2] *Ibid.*, **19**, 83.

An article has recently appeared by Macgregor and Archibald,[1] in which the preceding results and conclusions drawn from them are discussed. These authors show how it is possible to calculate the amount of the difference between the conductivity of the double salt and the sum of the conductivities of the constituents, when no double molecules can exist in the mixture of the two salts. We quote a few paragraphs from their paper that their point may be made clear.

"If we mix volumes v_1, v_2 of solutions of electrolytes 1 and 2, which have a common ion, and whose concentrations, ionization coefficients, and molecular conductivities at infinite dilution are, n_1, n_2; α_1, α_2; and $\mu\infty_1$, $\mu\infty_2$, respectively, the concentrations being so low that no appreciable change of volume occurs on mixing, and there being no formation of double salt, and if, after mixing, the ionization coefficients become α'_1, α'_2, respectively, the excess of the actual conductivity over the volume mean conductivity will be

$$[(\alpha'_1-\alpha_1)n_1v_1\mu\infty_1 + (\alpha'_2-\alpha_2)n_2v_2\mu\infty_2]/(v_1+v_2).$$

"This will not vanish unless (1) the solutions are infinitely dilute (all the α's equal to unity), or (2) the solutions are isohydric ($\alpha'_1-\alpha_1$ and $\alpha'_2-\alpha_2$ both equal to zero), or (3) the change of ionization and other quantities involved are appropriately related to one another."

They then proceed to calculate what the differences would be if no double salt existed in solution.

"For this purpose the $\mu\infty$'s and the α's of the above expression must be determined. The former may be found from the determinations of ionization coefficient and molecular conductivity made by Jones and Mackay. * * * The values which the ionization coefficients would have in the alum solutions, on the assumption of the presence of no double molecules, may be determined from the values of the ionization coefficients of the simple solutions observed by Jones and Mackay, by the method described by one of us in a former paper,[2] though the data are somewhat meagre for the purpose, and the results must therefore be used with caution.

---

[1] Phil. Mag., 46, 509.

[2] *Ibid.*, [5], 41, 276.

"Having obtained the requisite data in the ways indicated, we have calculated the amounts by which the conductivities of the alum solutions should differ from the arithmetic means of the conductivities of their mixture constituents, if no double salt were present as such; and we find that for solutions of $KAl(SO_4)_2$ and $KCr(SO_4)_2$ of dilution 12 litres per gram-molecule, the molecular conductivity should be less than the arithmetic mean of the molecular conductivities of the mixture constituents by about 0.4 and 0.7 per cent respectively. Jones and Mackay found that for these solutions the molecular conductivity was less than the arithmetic mean by 2.6 and 8.8 per cent respectively. Assuming that the available data are sufficient for the calculation, it is obvious not only that the conclusion of these observers with respect to the chromium alum seems to be substantiated, but that in the case of the potash alum, also, the result is such as would be accounted for by the existence of double salt in solution."

Jones and Mackay studied, also, one of the double chlorides, that of potassium and zinc, using the conductivity method in the same manner as with the double sulphates. As the results of their investigation upon this substance have not yet been published they are recorded in this place.

Rüdorff[1] distinguished two classes of double chlorides. Those which suffer decomposition in water solution, and those which remain undecomposed. The first class are to be regarded as double salts of the same type as the alums. The second class he regards as true binary compounds. The following examples of the first class are given:

$$2KCl + CuCl_2 + 2H_2O,$$
$$2NH_4Cl + CuCl_2 + 2H_2O,$$
$$2KCl + ZnCl_2 + H_2O,$$
$$KCl + MgCl_2 + 6H_2O,$$
$$2NaCl + CdCl_2 + 3H_2O,$$
$$BaCl_2 + CdCl_2 + 4H_2O.$$

It seemed of interest to study an example of this class by the conductivity method. For this purpose the double chloride of potassium and zinc was selected.

---

[1] Ber. d. chem. Ges., **21**, 3048 (1888).

Preparation.

In preparing the double chloride of potassium and zinc, potassium chloride, which had been twice crystallized, and was shown by the flame test to be free from sodium, was used. The zinc chloride used was tested and found to be free from impurities. The two chlorides were brought together in solution in the proportion necessary to form the double salt, and the solution evaporated to crystallization. The salt was separated as rapidly as possible from its mother-liquor, by the filter-pump, and dried under a press. A specimen dried at 130° was analyzed for zinc.

The analysis gave :

Percentage of zinc found	22.91
" calculated for $2KCl.ZnCl_2$	22.94

Conductivity Results obtained by Jones and Mackay for $2KCl.ZnCl_2$.

Volume. v.	μ_v at 25°. 1st series.	μ_v at 25°. 2nd series.	Mean of 1 and 2.
1.0	176.0	....	176.0
2.0	244.2	....	244.2
4.0	303.7	....	303.7
20.0	397.4	397.2	397.3
40.0	426.2	423.8	425.0
200.0	468.4	469.0	468.7
400.0	483.2	484.2	483.7
2000.0	504.0	504.6	504.3
4000.0	510.8	512.3	511.5
20000.0	516.8	509.0	512.9
40000.0	518.8	516.0	517.4

A comparison of the conductivity of the double salt with the conductivities of its constituents is given below. The values for zinc chloride and potassium chloride are interpolated from the tables of Kohlrausch,[1] and the temperature coefficient added, so that they obtain at 25°. The molecular conductivity of the zinc chloride is taken at the same volume as the double salt. That of potassium chloride is taken as twice the molecular conductivity of potassium chloride at one-half the volume of the double salt.

[1] Ann. d. Phys. (Wied.), **26**, 161 (1885).

Double Chloride of Zinc and Potassium.

Volume v of KCl.	KCl $2\mu_v$ 25°.	Volume v of $ZnCl_2$.	$ZnCl_2$. μ_v 25°.	Sum.	$2KCl.ZnCl_2$ observed. μ_v 25°.	Difference.
0.5	196.0	1.0	78.4	274.4	176.0	98.4
1.0	211.8	2.0	120.0	331.8	244.2	87.6
2.0	221.6	4.0	140.3	361.9	303.7	58.2
10.0	241.4	20.0	179.2	420.6	397.3	23.3
20.0	250.0	40.0	186.7	436.7	425.3	11.4
100.0	264.8	200.0	213.6	478.4	468.7	9.7
200.0	269.0	400.0	220.1	489.1	483.7	5.4
1000.0	275.4	2000.0	232.0	507.4	504.3	3.1
2000.0	277.6	4000.0	234.8	512.4	511.5	0.9
10000.0	279.0	20000.0	240.2	519.2	512.9	6.3
20000.0	280.0	40000.0	240.7	520.7	517.4	3.3

The foregoing comparison leaves no room for doubt as to the existence of this double salt as such in concentrated solution, while at a dilution of between 1000 and 2000 liters it is entirely dissociated into its constituents.

Conclusion.

Regarding the double chloride of zinc and potassium as a type of the class of dissociated double halides, the conclusion was drawn that these salts are present as such in their concentrated solutions. As compared with the alums, they show a greater degree of stability towards water in concentrated solutions, but, in dilute solutions, resemble them in becoming wholly dissociated into their component salts.

We have continued the investigation upon the double chlorides, thinking it desirable that a number of compounds should be studied. We at first repeated the above work on the double chloride of zinc and potassium. The compound was prepared and analyzed in exactly the same manner as described above. A standard solution was prepared and from this, directly or indirectly, all of the more dilute solutions were made. The conductivity measurements were made at 25°, so that the data are directly comparable with those given above. All of the water used in preparing the solutions was carefully purified by distilling from chromic acid and alkaline potassium permanganate, as already described.[1] We obtained the following results for the conductivity of the double salt, which are compared with the sum of the conductivities of the constituents, given in the preceding table. The differences given below are directly comparable with the differences in the above table :

---

[1] Ztschr. phys. Chem., **22**, 237.

$2KCl.ZnCl_2$.

Volume v.	μ_v at 25°.	Difference.
1.0	172.6	101.8
2.0	241.3	90.5
4.0	298.5	63.4
20.0	391.5	29.1
40.0	423.6	13.1
200.0	470.4	8.0
400.0	484.8	4.3
2000.0	510.5	—3.1
4000.0	512.0	0.4
20000.0	518.0	1.2
40000.0	520.0	0.7

Our results confirm those previously obtained, the slight differences being unquestionably due to experimental error.

We next prepared the double chloride of potassium and cadmium, $KCl.CdCl_2$, by bringing the constituent chlorides together in the proportion to form the double salt. The solution was carefully evaporated, the double salt separating without serious difficulty. It, however, requires more care to obtain this salt in pure condition than to obtain the corresponding zinc salt. The compound was freed from the mother-liquor by pressing between drying paper, and analyzed. The cadmium was determined by the carbonate method, with the result that the compound was shown to be pure. The results of the conductivity measurements of solutions of this salt are given in the following table, together with a comparison with the sum of the conductivities of the constituent chlorides.

Results for $KCl.CdCl_2$.

Volume v.	KCl μ_v 25°.	$CdCl_2$ μ_v 25°.	Sum.	$KCl.CdCl_2$ μv at 25°.	Difference.
2	111.27	46.88	158.15	116.35	41.80
4	113.74	64.70	178.44	144.42	34.02
8	118.68	83.27	201.95	171.79	30.16
16	122.33	102.55	224.88	198.18	26.70
32	125.91	122.09	248.00	223.87	24.13
64	127.97	143.13	271.10	250.53	20.57
128	130.80	163.55	294.35	276.21	18.14
256	132.28	182.21	314.49	303.03	11.46
512	133.99	197.94	331.93	325.45	6.48
1024	134.79	212.28	347.07	346.83	0.24

The double chloride of sodium and aluminium was particularly inviting for our work, since it is stated that this compound can be volatilized by heat, without decomposition. This substance is, thus, far more stable with respect to heat than other substances of its class, and it was therefore especially interesting to see whether it would show a corresponding relative stability with respect to water.

Several attempts were made to prepare the compound in quantity by the methods described, but none of them gave us a yield sufficient for our purpose. We then determined to mix solutions of the two chlorides in quantities just sufficient to form the double salt. The chloride of aluminium was prepared by dissolving pure aluminium hydroxide in hydrochloric acid, using a very slight excess of the hydroxide. The aluminium hydroxide was precipitated from pure potassium alum by ammonia, and the precipitate washed until it was free from potassium and ammonia. The hydroxide was washed by boiling the precipitate with large quantities of water, allowing it to settle, and successively decanting and filtering. The results obtained are given below:

Results for $NaCl.AlCl_3$.

Volume v.	$NaCl$ μ_v 25°.	$AlCl_3$ μ_v 25°.	Sum.	$NaCl.AlCl_3$ μ_v 25°.	Difference.
2.88	93.55	169.48	263.03	228.64	34.39
5.76	97.44	196.65	294.09	269.05	25.04
11.52	103.65	217.76	321.41	297.82	23.59
23.04	106.89	237.00	343.89	325.82	18.07
46.08	109.46	254.33	363.79	349.10	14.69
92.16	112.19	271.71	383.90	370.34	13.56
184.32	114.26	289.19	403.45	394.75	8.70
368.64	115.59	307.32	422.91	414.50	8.40

We then turned our attention to the double chloride of ammonium and mercury, ($2NH_4Cl.HgCl_2$). Mercuric chloride is, as is well known, very slightly dissociated by water. We wished to see whether results of the same general order as the above would be obtained, when one of the constituent chlorides remained in the solution for the most part in the molecular condition.

The double salt was prepared by bringing the constituent chlorides together in the proportion to form the salt, and carefully evaporating the solution until the double salt separated. The salt was quickly pressed between drying paper and analyzed. Analysis showed that the product which we used was pure. A solution of the strength desired was standardized, and from this all of the remaining solutions were prepared. The conductivity results obtained are given below :

Results for $2NH_4Cl.HgCl_2$.

Volume v.	NH_4Cl $2\mu_v$ 25°.	Volume v.	$HgCl_2$ μ_v 25°.	Sum.	$2NH_4Cl.HgCl_2$ μ_v 25°.	Difference.
2.5	221.7	5	0.79	222.49	195.5	26.99
5.0	230.0	10	1.17	231.17	213.0	18.17
10.0	238.64	20	1.60	240.24	227.73	12.51
20.0	247.24	40	2.48	249.72	240.68	9.04
40.0	252.64	80	3.80	256.44	251.93	4.51
80.0	257.52	160	6.02	263.54	260.70	2.84

Discussion of the Results.

It will be readily understood why twice the molecular conductivity of ammonium chloride, at one-half the dilution, is taken in the above table, if we consider that in the double salt there are two molecules of ammonium chloride to one of mercury chloride. The dilutions are so taken that they can be compared directly with the dilutions which we obtain in the solution of the double salt. These same remarks apply to the potassium chloride in the double salt with zinc, where there are two molecules of potassium chloride to one of zinc chloride. Before considering the final results obtained, it should be stated that the values of μ_v for potassium chloride, sodium chloride, and ammonium chloride, were obtained from the results of Kohlrausch's conductivity measurements, by interpolation ; the temperature coefficient being added in each case, transforming the results at 18° into results at 25°.

The values of the differences for the double chloride of potassium and cadmium are smaller than for the corresponding zinc salt at the same dilution, yet the same general relation obtains. The difference is largest in the most concentrated solution, and becomes smaller as the dilution increases, reaching zero at about 0.001 normal. It should be stated that our conductivity values for cadmium chloride differ appreciably from those of Grotrian.[1]

The differences are of the same order for the sodium aluminium chloride as for potassium cadmium chloride ; indeed, they are slightly less in the former case. The greater stability of the sodium aluminium chloride with respect to heat, therefore, does not manifest itself with respect to water. This compound is more dissociated in aqueous solution than substances of the same class which cannot be volatilized without decomposition.

The differences for the ammonium mercuric chloride are smaller, for the same dilution, than for either of the double chlorides thus far studied.

A comparison of the results obtained with the double sulphates with the results of this work, shows a much greater difference in the latter, between the sum of the conductivities of the constituents and the conductivity of the double salt. While this amounted at most to a few per cent with the alums, it is as great as 40 per cent for the double chloride of potassium and zinc, 26 per cent for the corresponding cadmium salt, 13 per cent for the double chloride of sodium and aluminium, and 12 per cent for the double chloride of ammonium and mercury. These differences for the double chlorides, as for the double sulphates, vanish at great dilution.

The conclusion that molecules of double salts exist in the more concentrated solutions, can be drawn with much greater confidence for the double chlorides than for the double sulphates. The former, under these conditions, are far more resistant to the dissociating action of water, than the latter.

It should be stated that this conclusion is directly in accord with the view of Remsen, that the double halides are to be regarded as well-defined chemical compounds. As measured by their power to resist the dissociating action of water, if the alums are chemical compounds, so much the more must we regard the double chlorides as such.

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[1] Ann. d. Phys. (Wied.), 18, 177 ; Ztschr. phys. Chem., 5, 481.

We attempted to apply the freezing-point method to the double chlorides, as had already been done in the case of the double sulphates. The results obtained were, however, not satisfactory. Work is now in progress in this line.

The study of other examples of double halides is now being made in this laboratory by Dr. Knight. We propose to examine by the conductivity, and perhaps the freezing-point method, a number of classes of double salts.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
January, 1899.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON UNDECYLAMINE AND PENTADECYLAMINE AND THE PREPARATION OF THE HIGHER AMINES OF THE ALIPHATIC SERIES[1].

BY ELIZABETH JEFFREYS.

Hofmann's[2] method of preparing amines by the action of bromine and potassium hydrate upon acid amides in aqueous solution according to

$$RCONH_2 + Br_2 + 4KOH = RNH_2 + 2KBr + K_2CO_3 + 2H_2O,$$

furnishes very good yields of the lower aliphatic amines, but as the molecular weight of the acid amide increases the yield of amine diminishes. This is due particularly to two secondary reactions, in one of which the bromine and alkali act upon the amines formed and produce nitrils according to the equation:

$$RCH_2NH_2 + 2Br_2 + 4NaOH = RCN + 4NaBr + 4H_2O.$$

By distilling the amine with steam as soon as it is formed, Hoogewerff and Van Dorp[3] succeeded in preventing the formation of nitrils.

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[1] Vide also a preliminary report, Ber. d. chem. Ges., **30**, 898.

[2] Hofmann: Ber. d. chem. Ges., **15**, 762.

[3] Hoogewerff and Van Dorp: Rec. trav. chim., **6**, 387.

In the other secondary reaction by which the yield of amine is diminished, acyl-alkylureas are formed:

$$2RCONH_2 + Br_2 + 2KOH = RNHCONHCOR + 2KBr + 2H_2O.$$

With increasing molecular weight of the acid amide, the formation of these acylureas is favored and in the higher series they are the chief product of the action of bromine and aqueous alkali on acid amides. By saponifying such ureas amines can be obtained, but the yield is small.

Amines higher in the series than heptylamine cannot be obtained with good yields by the Hofmann method. To prepare octylamine, Hoogewerff and Van Dorp[1] distilled the bromamide with lime and obtained 45 per cent of the theoretical yield of amine. This method involves the preparation of the bromamide and, as shown below, this is one of the main difficulties to overcome in the higher aliphatic series. Hoogewerff and Van Dorp's method in modified form is hardly feasible, therefore, for preparing amines of very high molecular weight.

Turpin[2] prepared heptadecylamine, $CH_3(CH_2)_{16}NH_2$, by converting stearic amide by means of aqueous potassic hydrate and bromine into stearyl-heptadecylurea and distilling the urea with lime. As but half the urea molecule is of avail in preparing the amine, the yield obtained was necessarily low (22 grams of heptadecylamine from 100 grams of stearamide), and as a ketone, stearon, is also formed in the same reaction, the isolation of the pure amine involves a tedious process.

Lengfeld and Stieglitz[3] having found that sodium methylate in methyl alcohol solution converts acid bromamides into urethanes according to

$$RCONHBr + CH_3ONa = CH_3NHCOOCH_3 + NaBr,$$

the work described in this paper was undertaken at the suggestion and carried on under the direction of Professor Stieglitz, to determine whether this reaction could not be utilized as a convenient method of preparing higher aliphatic amines, and also to determine, if possible, why, in the

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[1] Rec. trav. chim., **6**, 387.

[2] Ber. d. chem. Ges., **21**, 2488.

[3] This Journal, **15**, 215, 504; **16**, 270.

Hofmann reaction, the formation of ureas of the higher aliphatic series should be more favored than those of lower molecular weight.

The investigation was carried on by the use of palmitic, stearic, and lauric amides. All attempts to prepare palmitic and stearic bromamides proved unsuccessful.

The chloramides were, however, prepared with considerable difficulty and converted by treatment with sodium methylate into urethanes. As the preparation of the chloramides proved so difficult, an attempt was made to effect a rearrangement of the amides in alcohol solution without the isolation of the chlor- or bromamides.

The experiments proved successful, urethanes being formed in almost quantitative yield according to

$$RCONH_2 + Br_2 + 2NaOCH_3 = RNHCOOCH_3 + 2NaBr + HOCH_3.$$

As amines were obtained in excellent yield when the urethanes were distilled with lime, the investigation has proved entirely satisfactory in leading to as convenient a method of preparing the higher aliphatic amines, as that employed in obtaining the lower amines.

From the easily accessible lauric and palmitic amides, the hitherto unknown normal undecylamine and normal pentadecylamine were prepared in considerable quantity; and from undecylamine, undecyl alcohol, also heretofore unknown, was prepared.

In regard to the second object of investigation, it was soon found that in order to prevent the formation of urea, it is necessary that a rearrangement shall take place quickly, almost instantaneously, throughout the whole mass. In working with lauric amide, it was found necessary to mix the substances together as quickly as possible. When the sodium alcoholate solution was poured in small quantities into the flask containing the solution of amide and bromine, two-thirds of the product was found to be urea. The same result was obtained when the amide and sodium alcoholate solutions were mixed together and the bromine added, drop by drop, to the mixture. If, on the other hand, the sodium alcoholate solution was poured, all at once, into the bromine and amide solution, almost a quantitative yield of urethane was obtained.

Apparently when the reaction proceeds slowly, one molecule of the bromamide after suffering the Beckmann rearrangement, unites at once with a second molecule of acid amide which is still present under those conditions, to form urea according to:

$$RCONHBr + RCONH_2 + NaOCH_3 \rightarrow RCONHCONHR + NaBr + HOCH_3,$$

rather than with the alcohol to form a urethane.

The cause, therefore, of the formation of ureas when the higher amides are treated with bromine and aqueous alkali, according to Hofmann's method, lies undoubtedly in the fact, that, on account of their difficult solubility in aqueous solvents, the rearrangement of the acid amide takes place so slowly that there is always present a sufficient amount of amide to form a urea.

The inevitable conclusion to be drawn from the facts given was rather surprising, inasmuch as isocyanates, the probable intermediate products[1] in the Beckmann rearrangement,[2] under ordinary conditions, react much more readily with alcohols than with acid amides. Experiments were made by treating benzamide, in methyl alcohol solution, with phenyl isocyanate under varying conditions, and they invariably resulted in the formation of methylphenylurethane, not a trace of phenylbenzoylurea being formed.

According to Hoogewerff and Van Dorp bromformamides are the first intermediate products of the Beckmann rearrangement of acid bromamides, but chlorformanilide with a methyl alcohol solution of benzamide, under varying conditions, did not give any more phenylbenzoylurea than the isocyanate itself.[3]

The new method of converting acid amides into urethanes, by the action of bromine and sodium methylate, was found also to be applicable to the amides of the aromatic series. Since much time and labor are saved and the loss involved in the isolation of the dry bromamides is prevented, we can now class the urethanes among the most easily accessible bodies.

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[1] Hofmann: Ber. d. chem. Ges., 15, 412.

[2] Stieglitz: This JOURNAL, 18, 751.

[3] The question raised will be further investigated as it promises to throw more light on the theory of the Beckmann rearrangement of acid bromamides. Mr. Yates is studying the action of undecyl isocyanate on lauric amide, as lauric amide seems to show a marked tendency to form undecyllaurylurea when subjected to the action of the rearranging reagents.

This method was also tried in cases where the old method had either failed entirely or given poor results. The yields of urethanes obtained in ethyl alcohol solution were very much higher than those obtained by Swartz,[1] by the older method, but all attempts to effect a rearrangement of unsaturated acid amides, $RCH:CHCONH_2$, failed, because the unsaturated group is more reactive than the acid amide group.

For a similar reason salicylic amide, on account of the activity of the hydrogen of the benzene ring, due to the presence of the hydroxyl group, undergoes no rearrangement until the benzene ring has been brominated.

Experimental Part.

That acid chloramides can be used instead of acid bromamides in effecting the rearrangement to urethanes, was shown by the action of sodium methylate on benzchloramide. 1.2 gram (1 mol.) of benzchloramide was added to a solution of sodium methylate, obtained by dissolving 0.3 gram (2 atoms) of sodium in 12 grams of pure methyl alcohol. The reaction was complete after heating the mixture about five minutes on the water-bath. The excess of alkali was neutralized by acetic acid, the alcohol distilled and the residue recrystallized from hot water. The product obtained was identified by its melting-point (47°) and other properties as methylphenylurethane. The reaction takes place exactly as when benzbromamide is used.[2]

Palmitic Chloramide, $C_{15}H_{31}CONHCl$.—On account of the difficult solubility of palmitic amide, it was impossible to prepare palmitic bromamide, but the chloramide can be obtained in almost pure condition as follows: 10 grams of palmitic amide dissolved in about 400 cc. of alcohol were poured into about five times the calculated amount of hypochlorous acid, the acid having been prepared by passing chlorine into a 15 per cent solution of sodium carbonate, kept at a temperature of about —5°. A white precipitate was immediately formed, this being, evidently, the palmitic amide precipitated by the cold hypochlorous acid solution. Upon shaking the flask vigorously for a few minutes considerable heat was developed and the precipitate redissolved. On cooling, a white precipitate was deposited; this was filtered immediately and washed with a little ice-cold water. After it was dried on a clay plate for two or three hours, a chlorine determination was made by adding potassium iodide to an alcoholic solution of the chloramide, and acidifying and titrating with thiosulphate, the iodine being liberated according to:

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[1] This JOURNAL, 19, 295.

[2] Ber. d. chem. Ges., 19, 2274.

$$C_{15}H_{31}CONHCl + 2HI = C_{15}H_{31}CONH_2 + HCl + 2I.$$

I. 0.2046 gram substance gave 0.0238 gram chlorine.

II. 0.2026 gram substance gave 0.0236 gram chlorine.

	Calculated for $C_{16}H_{32}NOCl$.	Found.	
		I.	II.
Cl	12.26	11.65	11.65

Palmitic chloramide melts at 70°–71°. It is insoluble in water, difficultly soluble in cold alcohol and ligroin and readily soluble in benzene, chloroform and ether. The yield is almost quantitative.

Methyl Pentadecylcarbamate, $C_{15}H_{31}NHCO_2CH_3$, *from Palmitic Chloramide.*—To convert palmitic chloramide into urethane 5 grams of it was treated with 0.45 gram of sodium dissolved in 18 grams of methyl alcohol. The chloramide dissolved immediately in the alkaline solution, but it was necessary to boil the solution for twenty minutes before the action was complete. After distilling off the alcohol, the product remaining was washed with water and recrystallized from hot alcohol.

I. 0.4406 gram at 739.8 mm. and 23.5° gave 19.8 cc. nitrogen.

II. 0.4568 gram at 744.7 mm. and 22.5° gave 21.3 cc. nitrogen.

III. 0.1992 gram gave 0.5208 gram CO_2, and 0.2274 gram H_3O.

	Calculated for $C_{15}H_{31}NHCO_2CH_3$.	Found.	
		I.	II.
N	4.91	4.92	5.16
C	71.57	71.30	..
H	12.28	12.68	..

Methylpentadecylurethane is difficultly soluble in cold ligroin and in alcohol, but readily soluble in ether, chloroform and benzene. It crystallizes in leaflets and melts at 61°–62°.

Preparation of Urethanes Directly from Amides.

As the isolation of the chloramide proved to be very difficult, the following experiments were made to convert acid amides directly into urethanes without isolating the chlor- or bromamides.

Methyl Phenylcarbamate, $C_6H_5NHCOOCH_3$.—A solution of 3.8 grams (2 equiv.) of sodium in 95 grams of methyl alcohol was poured into a flask containing 10 grams of benzamide (1 equiv.), dissolved in 51 grams of methyl alcohol, and to this mixture, 13.2 grams (2 equiv.) of bromine were added. Some action took place in the cold, but it was necessary to heat the mixture for twenty minutes before the action was complete.

After recrystallization from hot water 5.9 grams of pure urethane were obtained. The reaction takes place in the same manner when the sodium methylate solution is added to the mixture of amide and bromine solution.

Methyl m-Nitrophenylcarbamate, $NO_2C_6H_4NHCOOCH_3$.—3.8 grams (1 equiv.) of *m*-nitrobenzamide were dissolved in 16 grams of methyl alcohol, and to this were added 4 grams (2 equiv.) of bromine and 1.1 gram (2 equiv.) of sodium dissolved in 28 grams of methyl alcohol. The alcohol was allowed to evaporate at ordinary temperature and the residue shaken up with hydrochloric acid, to remove the small quantity of *m*-nitraniline formed, and then recrystallized from chloroform. The urethane was recognized by its crystal form and melting-point (147°–149°) as being identical with the one obtained by Folin.[1] The yield obtained was 91 per cent of theory.

Methyl Pentadecylcarbamate, $C_{15}H_{31}NHCOOCH_3$, *from Palmitic Amide.*—25.5 grams (1 mol.) of palmitic amide, dissolved by warming in 69 grams of methyl alcohol, were mixed with a solution of 4.6 grams (2 atoms) sodium in 115 grams of methyl alcohol and 16 grams (1 mol.) of bromine added.

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[1] Folin: This JOURNAL, 19, 323.

The mixture was heated on the water-bath for about ten minutes. After adding a few drops of acetic acid to neutralize the excess of alkali, the alcohol was distilled off, and the remaining product washed thoroughly with water to remove the sodium bromide. It was then dissolved in ligroin to separate the urethane from some unchanged palmitic amide (m. p. 104°), which is difficultly soluble in ligroin. When recrystallized twice from alcohol, the urethane melted at 61°–62°, agreeing with that of the pentadecylurethane obtained by the action of sodium methylate upon palmitic chloramide. The yield is 83–94 per cent of the calculated quantity.

Its identity was further shown by an analysis.

0.383 gram at 752.6 mm. and 21.5° gave 17.9 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCOOCH_3$.	Found.
N	4.91	5.25

Normal Pentadecylamine, $CH_3(CH_2)_{14}NH_2$.—Pentadecylamine can be prepared by heating pentadecylurethane with concentrated hydrochloric acid (five hours in a sealed tube to 200°) or with concentrated sulphuric acid (one hour to 110°–120° in an open flask) and then heating with alcoholic potash and distilling. The best method of preparing the amine is to distil the urethane with about three and one-half times its weight of slaked lime, the amine being obtained quantitatively according to the equation :

$$C_{15}H_{31}NHCOOCH_3 + Ca(OH)_2 = C_{15}H_{31}NH_2 + CaCO_3 + CH_3OH.$$

Pentadecylamine Hydrochloride, $CH_3(CH_2)_{14}NH_3Cl$.—This salt is best prepared by dissolving the free amine (obtained by distilling pentadecylurethane with lime) in alcohol, adding an excess of concentrated hydrochloric acid, and evaporating to dryness on the water-bath. It was purified by washing it thoroughly with ether, then dissolving it in a small quantity of alcohol and precipitating with ether.

I. 0.3446 gram substance at 750.3 mm. and 23° gave 17.2 cc. nitrogen.

II. 0.4086 gram substance at 747 mm. and 16° gave 19.5 cc. nitrogen.

III. 0.2788 gram substance gave 0.6990 gram CO_2, and 0.328 gram H_2O.

IV. 0.2244 gram substance gave 0.5604 gram CO_2, and 0.2659 gram H_2O.

	Calculated for $C_{15}H_{31}NH_3Cl$.	Found. I.	II.
N	5.31	5.55	5.43
C	68.31	68.37	68.10
H	12.90	13.07	13.16

Pentadecylamine hydrochloride crystallizes in glistening leaflets ; it is very soluble in alcohol, but insoluble in ether, ligroin, and water. It decomposes without melting at 200°.

Pentadecylamine Chlorplatinate, $(C_{15}H_{31}NH_3)_2PtCl_6$, was prepared by adding a solution of chlorplatinic acid to an alcoholic solution of pentadecylamine. A yellow body was precipitated which is slightly soluble in alcohol, insoluble in water and decomposes without melting when heated above 205°.

0.5356 gram gave 0.1218 gram of platinum.

	Calculated for $(C_{15}H_{31}NH_3)_2PtCl_6$.	Found.
Pt	22.57	22.73

Monopentadecylurea, $C_{15}H_{31}NHCONH_2$. — The monourea furnishes an easy method for the rapid and certain identification of pentadecylamine or its hydrochloride. Molecular quantities of pentadecylamine hydrochloride dissolved in alcohol, and potassium cyanate, dissolved in as small a quantity of water as possible, were mixed together and evaporated to dryness on the water-bath. The compound formed was washed with water and recrystallized from hot alcohol.

0.2158 gram substance at 747.1 mm. and 21.5° gave 20.2 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCONH_2$.	Found.
N	10.37	10.45

Monopentadecylurea is a white substance crystallizing in leaflets and melting at 109° ; it is insoluble in ligroin but readily soluble in hot alcohol. It was used most frequently in identifying the new amine.

Pentadecylamine, $CH_3(CH_2)_{14}NH_2$.—The free amine is best prepared as follows: 70 grams of lime, to which has been added 30 grams of water and 20 grams of pentadecylurethane are thoroughly mixed together and distilled from a porcelain, or hard glass retort of 300 cc. capacity. The receiver was kept in cold water. The product formed was dissolved in ligroin, and dried with caustic potash. The ligroin solution was separated from the caustic potash by filtering it with a siphon filter. The amine was then heated on the water-bath for a couple of hours over sodium, and finally distilled over sodium into a second distilling-flask, from which it was redistilled.

I. 0.3488 gram at 751.8 mm. and 13.7° gave 17.1 cc. nitrogen.

II. 0.4186 gram at 735.4 mm. and 15.5 gave 21.1 cc. nitrogen.

	Calculated for $C_{15}H_{31}NH_2$.	Found. I.	II.
N	6.16	5.75	5.69

When the free amine is weighed it absorbs carbon dioxide and water from the air with such avidity that it is impossible to get very good figures. In order to obtain a more exact analysis, the specimen analyzed was converted into the hydrochloride, and a determination of the hydrogen, carbon and nitrogen made (see second analysis of pentadecylamine hydrochloride).

Pentadecylamine is a white substance crystallizing in leaflets, melting at 36.5° and boiling at 298°–301° at ordinary pressure; it has a peculiar odor, dissolves in all the organic solvents, and combines with acids, but does not dissolve in them. By working carefully, almost a quantitative yield can be obtained.

Benzoylpentadecylamine, $C_{15}H_{31}NHCOC_6H_5$.—A calculated quantity (1 mol.) of benzoyl chloride was added to an ether solution of pentadecylamine (2 mol.). In order to get all the amine in solution, it was necessary to heat it to drive off any carbon dioxide absorbed, as the carbonate is not soluble in ether. The ether mixture was shaken up with a weak solution of caustic soda and when no further odor of benzoyl chloride was perceptible, it was washed two or three times with water and the ether distilled.

The compound obtained crystallizes in needles and melts at 78°; it is soluble in ether, alcohol and benzene.

For analysis it was recrystallized from benzene.

I. 0.4552 gram substance at 743.3 mm. and 17° gave 18.2 cc. nitrogen.

II. 0.4368 gram substance at 746.1 mm. and 17.3° gave 17.1 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCOC_6H_5$.	Found. I.	II.
N	4.22	4.59	4.44

All the analytical data obtained for the compound formed when pentadecylurethane is distilled with slacked lime, as well as those obtained for its derivatives, indicate that it is a primary amine formed according to:

$$C_{15}H_{31}NHCO_2CH_3 + Ca(OH)_2 = C_{15}H_{31}NH_2 + CaCO_3 + HOCH_3.$$

As Nölting[1] observed that methylphenylurethane, $C_6H_5NH CO_2CH_3$, gives on distilling with lime (unslacked) monomethylaniline according to:

$$C_6H_5NHCO_2CH_3 + CaO = C_6H_5NHCH_3 + CaCO_3,$$

and the analytical figures for derivatives of pentadecylamine, $C_{15}H_{31}NH_2$, and methylpentadecylamine, $C_{15}H_{31}NHCH_3$, lie rather close together, some reactions were tried which prove beyond any doubt that the amine prepared by me is a primary amine; with carbon disulphide it gives a mustard oil, $C_{15}H_{31}N{=}CS$; by the action of phosgene the isocyanate, $C_{15}H_{31}NCO$, is obtained and by the action of sodium nitrite on the hydrochloride of the amine, it is converted into normal primary pentadecyl alcohol, $C_{15}H_{31}OH$.

Pentadecylamine Pentadecyl Dithiocarbamate, $(C_{15}H_{31}NH) CS_2NH_3C_{15}H_{31}$, was obtained when an excess of carbon disulphide was added to an ether solution of pentadecylamine. A white precipitate was at once formed, which, when filtered and dried, melted at 99°. The substance was not analyzed, but was heated in a sealed tube for twenty hours at 100°.

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[1] Ber. d. chem. Ges., **21**, 3155.

Hydrogen sulphide was split off, and the dithiocarbamate converted into dipentadecylthiourea according to :

$$(C_{15}H_{31}NH)CS_2NH_3C_{15}H_{31} = (C_{15}H_{31}NH)_2CS + H_2S.$$

Dipentadecylthiourea was recrystallized by dissolving it in alcohol and precipitating it with water. It melts at 88·5°.

0.2142 gram gave 0.0984 gram barium sulphate (Carius' method).

	Calculated for $(C_{15}H_{31}NH)_2CS$.	Found.
S	6.45	6.30

Pentadecyl Mustard Oil, $C_{15}H_{31}NCS$, was prepared by heating pentadecylamine in solution in absolute alcohol with an excess of carbon disulphide :

$$C_{15}H_{31}NH_2 + CS_2 = C_{15}H_{31}NCS + H_2S.$$

This simple method seems to be a general one for preparing mustard oils from the higher aliphatic amines, since it succeeded with pentadecylamine as well as with heptadecylamine.[1] It was necessary to boil the alcoholic mixture for two days, at the end of which time no further odor of hydrogen sulphide could be detected. On evaporating the alcohol, a solid and an oil remained in the flask. The oil was dissolved in ligroin, and the solid remaining undissolved was identified as dipentadecylthiourea (m. p. 88.5°). As the oil was found to be impure and as it decomposes on distilling *in vacuo*, no analysis of the compound could be obtained, but it was identified as being chiefly pentadecyl mustard oil, $C_{15}H_{31}NCS$, by its action on amines. With aniline it gives phenylpentadecylthiourea according to :

$$C_{16}H_{31}NCS + C_6H_5NH_2 = C_{15}H_{31}NHCSNHC_6H_5,$$

and warmed with pentadecylamine, it yields dipentadecylthiourea.

Phenylpentadecylthiourea, $C_{15}H_{31}NHCSNHC_6H_5$, was obtained when molecular quantities of the mustard oil, dissolved in alcohol and aniline, were mixed together, and the solution boiled for ten or fifteen minutes on the water-bath. A few drops of acetic acid were added and the alcohol distilled. After recrystallizing the residue several times from alcohol, the thiourea obtained was found to melt at 79°.

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[1] Turpin: Ber. d. chem. Ges., **21**, 2486.

The same compound was also prepared by adding to pentadecylamine the calculated amount of phenyl mustard oil, and heating the mixture for a few minutes on the water-bath. After recrystallizing from alcohol, the substance obtained by this method was found to melt at 79°. A mixture of the two melted sharply at 79°, showing them to be identical and leaving no doubt as to the constitution of the thiourea.

0.267 gram substance at 24° and 747 mm. gave 19 cc. nitrogen.

	Theory for $C_{22}H_{38}N_2S$.	Found.
N	7.73	7.84

To convert the mustard oil into dipentadecylthiourea, it was added to a calculated quantity of pentadecylamine, dissolved in alcohol, and heated for a short time. The thiourea obtained in this manner, when recrystallized from alcohol, melts at 88.5° and agrees in every respect with the dipentadecylthiourea previously prepared.

Pentadecylurea Chloride, $C_{15}H_{31}NHCOCl$.—An effort was made to obtain the urea chloride by the method employed by Gattermann[1] in preparing the lower alkyl urea chlorides.

Some pentadecylamine hydrochloride was heated in an oil-bath to 150° and a slow stream of phosgene passed over it for several hours. A small quantity of liquid was formed, which, when treated with ammonia, gave a substance melting at 109° and identified as monopentadecylurea, thus proving the liquid to be the isocyanate expected. A small amount of dipentadecylurea was also formed, but the greater portion of the amine hydrochloride remained unchanged. As the yield of isocyanate obtained by this method was very unsatisfactory, 4 grams of pentadecylamine hydrochloride and 8 cc. of liquid phosgene were heated together in a sealed tube for ten hours at 100°. On cooling, the excess of phosgene was allowed to escape and a colorless solid mass remained in the tube. This was dissolved in as small a volume as possible of benzene dried by sodium, and the small quantity of unchanged amine hydrochloride was precipitated by dry ligroin. After filtering from the hydrochloride, the benzene and ligroin were distilled while a current of dry hydrogen chloride was passed through the flask. A white solid remained, which, after drying on a clay plate for forty minutes in a vacuum desiccator, was analyzed and found to be pure pentadecylurea chloride formed according to:

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[1] Ann. Chem. (Liebig), **244**, 33.

$$C_{15}H_{31}NH_3Cl + COCl_2 = C_{15}H_{31}NHCOCl + 2HCl.$$

0.3208 gram at 752.8 mm. and 22° gave 14.5 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCOCl$.	Found.
N	4.83	5.07

The urea chloride reacts readily with alcohol and amines. Whereas other urea chlorides as chlorformanilide[1] and chlorformnitranilide[2] and chlorformmethyl-[3] and ethyl amides are quite unstable, decomposing rapidly at 60°–100° into hydrochloric acid and isocyanate, chlorformpentadecylamide, is quite a stable body losing its hydrogen chloride with such difficulty that even after it was heated at 100°–150° for several hours in a stream of dry air, the hydrogen chloride had not been entirely split off. This greater stability of chlorformamides of high molecular weight is probably due to the greater basicity of the compounds on account of the increased positive character of the radical as its weight increases.

Pentadecyl Isocyanate, $C_{15}H_{31}NCO$, was prepared most readily by dissolving the urea chloride in benzene and heating it with calcium oxide, the isocyanate being liberated according to:

$$2C_{15}H_{31}NHCOCl + 2CaO = 2C_{15}H_{31}NCO + CaCl_2 + Ca(OH)_2.$$

When a test showed that the hydrogen chloride had been entirely removed, the solution was filtered from the calcium salts and the benzene distilled, the last traces being removed at reduced pressure. An oil with a slight brownish tint remained. Placed in a freezing-mixture, it solidified and then melted at 8°–14°. All precautions having been taken to prepare the cyanate in a pure condition, it was analyzed without further purification.

0.3192 gram at 745 mm. and 18° gave 15.1 cc. nitrogen.

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[1] Hentschel: Ber. d. chem. Ges., **18**, 1178; Lengfeld and Stieglitz: This JOURNAL, **16**, 75.

[2] Swartz: This JOURNAL, **19**, 311; Folin: *Ibid.*, **19**, 338.

[3] Gattermann: *Loc. cit.*

	Calculated for $C_{15}H_{31}NCO$.	Found.
N	5.53	5.35

The identity of the isocyanate was confirmed by converting it, by means of aniline, into pentadecylphenylurea.

Pentadecylphenylurea, $C_{15}H_{31}NHCONHC_6H_5$. — Molecular quantities of pentadecyl isocyanate and freshly distilled aniline dissolved in benzene were heated together for a few minutes. After adding a few drops of acetic acid the benzene was distilled off, and the product recrystallized from hot alcohol. The urea melts at 94°.

0.1280 gram gave 0.1276 gram H_2O, and 0.3576 gram CO_2.

	Calculated for $C_{22}H_{38}N_2O$.	Found.
H	10.98	11.07
C	76.30	76.18

Dipentadecylurea, $(C_{15}H_{31}NH)_2CO$, was obtained in pure condition by heating together 1.1 gram (1 mol.) of pentadecyl isocyanate and 1 gram (1 mol.) of pentadecylamine and recrystallizing from alcohol.

0.3074 gram at 18° and 749.1 mm. gave 15.1 cc. nitrogen.

	Theory for $(C_{15}H_{31}NH)_2CO$.	Found.
N	5.83	5.89

The same substance was also obtained by desulphurizing the thiourea in alcohol solution with mercuric oxide.

Dipentadecylurea is difficulty soluble in hot alcohol; it crystallizes in small needles and melts at 113°.

Ethyl Pentadecylcarbamate, $C_{15}H_{31}NHCOOC_2H_5$, was prepared by boiling pentadecyl isocyanate with ethyl alcohol. It is a white crystalline body melting at 54°, and was found to be identical with the urethane obtained by a rearrangement of palmitic amide when bromine and sodium ethylate act upon it in solution in ethyl alcohol, as described below.

Pentadecyl Alcohol, $C_{15}H_{31}OH$.—Ten grams (1 mol.) of pentadecylamine hydrochloride was dissolved in alcohol and 2.6 grams (1 mol.) of sodium nitrite, dissolved in water, added to the solution. Only a small quantity of gas was generated and a white precipitate separated out. A small portion of this precipitate was filtered off and dried on a clay plate. It was found to decompose with a rapid evolution of gas when heated to 60°. Water was then poured into the flask containing the remaining portion and the mixture boiled until gas ceased to come off. The oil, which was formed, was taken up by ether, and hydrogen chloride gas passed through the ether solution.

A white substance separated out, which was identified as unchanged pentadecylamine hydrochloride. It was found that, if the water solution is kept neutral by adding a few drops of hydrochloric acid from time to time, when necessary, the amine will all be used up in the reaction. After removing the ether by distillation, the alcohol was purified as follows: It was poured into a hot concentrated solution of calcium chloride then taken up by ether, the ether distilled and the residue boiled with water. The oil was again taken up by ether and upon removing the ether, a mixture of oil and solid remained in the flask. By dissolving the mixture in a small quantity of alcohol and placing the flask in a freezing-mixture, the oil remained in solution and the solid crystallized out.

By filtering quickly while cold, a white crystalline body melting at 45°–46° was obtained, the melting-point agreeing with that obtained by Simonini[1] for pentadecyl alcohol; the greater portion of the product was an oil, which undoubtedly consisted principally of the hydrocarbon, $C_{15}H_{30}$ (see below under undecylamine). The pentadecyl alcohol obtained was further identified by converting it into:

Pentadecyl Phenylcarbamate, $C_6H_5NHCOOC_{15}H_{31}$, which was formed when the alcohol and phenyl isocyanate were mixed together and allowed to remain in a desiccator for twelve hours. As some of the isocyanate remained unchanged, the substance was boiled with water and, in this way, the excess of isocyanate converted into diphenylurea. As diphenylurea is insoluble in ligroin, and the urethane is readily soluble, the two substances were easily separated. For analysis the urethane was recrystallized from ligroin.

0.2668 gram substance at 744.2 mm. and 19° gave 9.6 cc. nitrogen.

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[1] Monatshefte, 14, 81.

	Theory for $C_6H_5NHCOOC_{15}H_{31}$.	Found.
N	4.03	4.04

Pentadecylphenylurethane crystallizes in leaflets ; it is soluble in all the organic solvents and melts at 72°. On account of its comparatively high melting-point and the ease with which it can be purified, it serves as a better means of identifying pentadecyl alcohol than any other known derivative.

The reactions studied prove conclusively that the amine obtained by distilling pentadecylurethane with slaked lime is the primary normal pentadecylamine, $C_{15}H_{31}NH_2$. In order to find whether the methods described for obtaining urethanes and amines are generally for amides of high molecular weight, the same reactions were carried out with stearic and lauric amides.

Stearic Chloramide, $C_{17}H_{35}CONHCl$, was prepared in the same manner as palmitic chloramide. As stearic amide is very difficulty soluble in cold alcohol, it is difficult to obtain the chloramide free from unchanged amide, from which it could not be separated.

0.2002 gram gave 0.0204 gram chlorine.

	Theory for $C_{17}H_{35}CONHCl$.	Found.
Cl	11.18	10.20

The analysis shows that the product obtained was not absolutely pure. No further effort was made to obtain it in pure condition, but it was further identified by converting it into the urethane, which can easily be separated from the amide by means of ligroin, in which the amide is insoluble. The urethane melts at 63°–64° and crystallizes in leaflets, and is identical with methylheptadecylurethane obtained by the direct method.

Methyl Heptadecylcarbamate, $C_{17}H_{35}NHCO_2CH_3$, was obtained directly from the amide by means of bromine and sodium methylate in solution in methyl alcohol, as described for preparing methylpentadecylurethane. The yield is 97 per cent of the theoretical. It was purified for analysis by recrystallization from ligroin and alcohol.

0.4584 gram substance gave 19.6 cc. nitrogen at 740.8 mm. and 20.5°.

	Calculated for $C_{17}H_{35}NHCOOCH_3$.	Found.
N	4.47	4.72

Heptadecylamine, $CH_3(CH_2)_{16}NH_2$, was prepared by distilling methylheptadecylurethane with three or four times its weight of slaked lime. Almost a quantitative yield of amine was obtained, 100 grams of amide giving about 82 grams of amine. Turpin[1] obtained only 22 grams of this amine from 100 grams of stearic amide by using aqueous alkali and bromine.

A portion of the amine dissolved in alcohol was evaporated to dryness on the water-bath with concentrated hydrochloric acid. The substance thus obtained is soluble in alcohol, insoluble in ether and decomposes at 200° without melting. It corresponds in every respect with the heptadecylamine hydrochloride obtained by Turpin.

To further identify the amine, the hydrochloride was dissolved in alcohol and evaporated to dryness on the water-bath with the molecular quantity of potassium cyanate, dissolved in water. The body obtained, when recrystallized several times from alcohol, melts at 109° and corresponds in appearance and melting-point to the monoheptadecylurea described by Turpin.

Methyl Undecylcarbamate, $C_{11}H_{23}NHCO_2CH_3$.—To 6 grams (1 equiv.) of lauric amide dissolved in 21 grams of pure methyl alcohol, and 1.4 grams (2 equiv.) of sodium dissolved in 35 grams of methyl alcohol 4.8 grams (2 equiv.) of bromine was added and the mixture boiled for about five minutes. After neutralizing the alkali with acetic acid, the alcohol was distilled and the residue was washed with water, dried, and shaken up with ligroin. A large portion remained undissolved; this was filtered off and the ligroin distilled. A white substance crystallizing in leaflets and melting at 45°–47° (near the melting-point to be expected for a methyl undecylurethane) was obtained. Although this urethane had been prepared in exactly the same manner as the other aliphatic urethanes described above, which were obtained in almost quantitative yield, it was found that, in this case, the yield was only about one-third of the theoretical. The substance insoluble in ligroin was then examined and found to have the melting-point 102°, corresponding very closely with that of lauric amide; but when mixed with some of the pure amide, the melting-point was considerably depressed, showing it to be a different substance. This and the high melting-point indicated that the compound might be undecyllaurylurea, $C_{11}H_{23}NHCONHCOC_{11}H_{23}$, of the class of acylureas, whose formation interfered with the application of Hofmann's reaction, in aqueous solution, to higher aliphatic acid amides. This conclusion was verified as described below. For the time being, efforts were directed chiefly to obtaining a better yield of urethane.

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[1] *Loc. cit.*

In a second experiment the solution of sodium methylate was added in small quantities to the solution of the mixture of bromine and amide. The yield of urethane obtained was no better than before.

The third time the experiment was carried out as follows: 6 grams ($1\frac{1}{4}$ mol.) of bromine was added to 6 grams (1 mol.) of lauric amide dissolved in 27 grams of methyl alcohol, and a solution of 1.8 grams ($2\frac{1}{2}$ atoms) of sodium in 45 grams of methyl alcohol poured at once into the mixture. This time no urea was formed, but a quantitative yield of urethane was obtained. These experiments were repeated a great number of times and in every case, when the entire quantity of sodium methylate was added at once to the solution of the amide and bromine undecylurethane was obtained in excellent yield. If a portion of the solution of sodium methylate was added and but a second elapsed before the remainder was poured into the mixture, the product formed was principally urea.

To obtain the undecylurethane perfectly pure for analysis, it was dissolved in ligroin, in order to separate it from urea and unchanged amide, and then, after removing the ligroin, it was distilled at reduced pressure in an Anschütz distilling-flask.

I. 0.176 gram gave 0.4364 gram CO_2, and 0.187 gram H_2O.

II. 0.2412 gram gave 0.6008 gram CO_2, and 0.2588 gram H_2O.

III. 0.3154 gram gave 17.6 cc. nitrogen at 759.5 mm. and 19.5°.

	Calculated for $C_{11}H_{23}NHCOOCH_3$.	Found. I.	II.	III.
C	68.12	67.62	67.93	....
H	11.78	11.80	11.92	....
N	6.11	....	....	6.39

Undecylurethane is but slightly soluble in water and is much more soluble in the organic solvents than the other aliphatic urethanes obtained. It melts at 45°–47° and can be distilled at reduced pressure without decomposition.

Undecyllaurylurea, $C_{11}H_{23}NHCONHCOC_{11}H_{23}$.—The substance described above as one of the products of the reaction in the first attempt to prepare undecylurethane, was purified by recrystallization from hot ligroin. Analysis showed it to be undecyllaurylurea as expected.

0.2176 gram gave 14.2 cc. nitrogen at 744 mm. and 20°.

	Calculated for $C_{24}H_{48}N_2O_2$.	Found.
N	7.07	7.32

Undecyllaurylurea is difficultly soluble in all the organic solvents in the cold, but dissolves quite readily in hot alcohol. It crystallizes in leaflets and melts at 105°.

To identify the urea more completely it was saponified by heating it with concentrated hydrochloric acid in a sealed tube for five hours at 200°, undecylamine hydrochloride and lauric acid being formed according to :

$$C_{11}H_{23}NHCONHCOC_{11}H_{23} + 2H_2O + 2HCl = \\ C_{11}H_{23}NH_3Cl + C_{11}H_{23}COOH + NH_4Cl + CO_2.$$

The undecylamine hydrochloride was recognized by its insolubility in ether, decomposition at 190° without melting; and by the urea obtained by treating it with potassium cyanate. The melting-point of the urea (110°) did not change when it was mixed with some of the analyzed specimen of undecylurea.

Normal Undecylamine Hydrochloride, $CH_3(CH_2)_{10}NH_3Cl$.—8 grams of methylundecylurethane were distilled with 28 grams of slaked lime. The product obtained was dissolved in alcohol, concentrated hydrochloric acid added and evaporated to dryness on the water-bath. It was purified by washing it with ether, dissolving it in a small quantity of alcohol and reprecipitating it with ether. Like the other amine hydrochlorides obtained, it is insoluble in ether and decomposes without melting. It crystallizes in bright glistening plates.

I. 0.3246 gram gave 19.9 cc. of nitrogen at 741.5 mm. and 20.5°.

II. 0.2088 gram gave 0.4864 gram CO_2, and 0.2370 gram H_2O.

	Calculated for $C_{11}H_{23}NH_3Cl$.	Found. I.	II.
N	6.74	6.87	....
C	63.61	....	63.53
H	12.53	....	12.61

Undecylamine Chlorplatinate, $(C_{11}H_{23}NH_3)_2PtCl_6$, can be obtained from the amine hydrochloride by dissolving it in alcohol, adding an excess of chlorplatinic acid, and precipitating the chlorplatinate from the alcoholic solution by means of water. The chlorplatinate is a yellow crystalline body, quite soluble in alcohol and insoluble in water. It decomposes when heated to 190°.

0.4468 gram chlorplatinate gave 0.1162 gram platinum.

	Calculated for $(C_{11}H_{23}NH_3)_2PtCl_6$.	Found.
Pt	25.93	26.03

Undecylamine can be most readily identified by converting the hydrochloride into monoundecylurea. The hydrochloride, best dissolved in alcohol, and a calculated quantity of potassium cyanate, dissolved in a small quantity of water, were mixed together and evaporated to dryness. The product was thoroughly washed with water and recrystallized several times from hot alcohol. It melts at 110° and crystallizes in prismatic needles.

As the body is easily obtained in a pure condition, it serves as the most practical test for undecylamine.

0.1466 gram at 755.2 mm. and 19° gave 17 cc. of nitrogen.

	Calculated for $C_{11}H_{23}NHCONH_2$.	Found.
N	13.08	13.25

Normal Undecylamine, $CH_3(CH_2)_{10}NH_2$.—In order to obtain the free amine perfectly pure, the product obtained by distilling methylundecylurethane with lime is treated as follows: The amine is dissolved in ligroin, the solution dried with solid potassic hydrate and filtered by the use of a siphon filter, and then further dried by heating for about two hours on the water-bath with sodium, and finally distilled over sodium.

As considerable difficulty was experienced in distilling the body on account of its foaming, it was necessary to use a much larger distilling-flask than usual. After distilling the substance from the sodium, a second distillation can be made without any difficulty. A small quantity of the body distilled at 227°–232° but the greater portion gave a constant boiling-point of 232°.

In making a nitrogen determination, it was necessary to use a very long furnace in order to keep the portion of the tube containing the substance perfectly cold, while the other end was being heated; otherwise the substance was carried over by the carbon dioxide before the tube was sufficiently hot. When cold, the substance existed as a carbonate and in that form it is not volatile.

I. 0.2508 gram substance at 749.7 mm. and 22° gave 21 cc. nitrogen.

II. 0.2642 gram substance at 744.4 mm. and 24° gave 20.6 cc. nitrogen.

	Calculated for $C_{11}H_{23}NH_2$.	Found.	
		I.	II.[1]
N	8.18	9.31	8.56

The amine was also dissolved in alcohol and titrated with hydrochloric acid, lacmoid being used as an indicator.

I. 0.1978 gram required 11.35 cc. of $\frac{N}{10}$ hydrochloric acid.

Calculated.	Found.
11.56 cc.	11.35 cc.

0.2528 gram required 14.58 cc. $\frac{N}{10}$ hydrochloric acid.

Calculated.	Found.
14.78 cc.	14.58 cc.

At ordinary temperature undecylamine is a colorless liquid; it melts at 15° and boils at 232° under 742 mm. pressure. Like the other amines obtained, it absorbs carbon dioxide and water from the air. In the form of a carbonate it is a white solid.

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[1] I was made in a short furnace and II in a long one.

An effort was made to obtain undecylamine directly by the Hofmann method, proceeding as follows: Molecular quantities of bromine and lauric amide, dissolved in a small quantity of alcohol were mixed together and poured into a hot ten per cent solution of caustic potash. A very small quantity of amine was formed, but the principal part of the product was undecyllaurylurea (m.p. 105°).

Benzoylundecylamine, $C_{11}H_{23}NHCOC_6H_5$.—The free amine gives a characteristic benzoyl derivative, which was obtained when a quantity of undecylamine (2 mols.) was dissolved in ether, and the calculated amount of benzoyl chloride (1 mol.) added. The amine hydrochloride formed was filtered, and the ether solution shaken up with a dilute caustic potash solution until no further odor of benzoyl chloride could be detected. After washing with water, the ether was distilled, and the residue dissolved in benzene and precipitated with ligroin.

0.2644 gram at 739 mm. and 20° gave 12.7 cc. of nitrogen.

	Calculated for $C_{11}H_{23}NHCOC_6H_5$.	Found.
N	5.09	5.34

Benzoylundecylamine is very soluble in alcohol, ether, and benzene, but difficultly soluble in ligroin. It crystallizes in needles and melts at 60°.

Action of Sodium Nitrite on Undecylamine Hydrochloride.

Normal undecyl alcohol being one of the few unknown primary normal alcohols, and normal undecylamine being easily prepared in quantity, as described above, it was used as a means of obtaining the alcohol. When sodium nitrite acts upon undecylamine hydrochloride secondary reactions take place, besides the usual action of nitrous acid upon the amines.

In trying the action of sodium nitrite upon primary propyl and butyl amines, V. Meyer and Fr. Forster[1] found that four products were obtained. The primary alcohol was formed in the usual manner:

$$RNH_2 + HONO = ROH + N_2 + H_2O;$$

an unsaturated hydrocarbon as follows:

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[1] Ber. d. chem. Ges., 9, 529; 10, 130.

$$RCH_2CH_2NH_2 + HONO \rightarrow RCH{=}CH_2 + N_2 + 2H_2O;$$

a secondary alcohol by addition of water to the unsaturated hydrocarbon,

$$RCH{=}CH_2 + HOH \rightarrow RCHOHCH_3;$$

and a nitrosodialkylamine whose method of formation was explained by Linnemann,[1] who had previously obtained the same body by the same reaction. He assumes that amine nitrite is formed as an intermediate product, the formation of the nitrosamine then taking place according to the equation :[2]

$$2RNH_3NO_2 = R_2N.NO + N_2 + 3H_2O.$$

There is reason to believe that, when sodium nitrite acts upon undecylamine, corresponding products are formed, although but two of them were thoroughly investigated.

Normal Undecyl Alcohol, $CH_3(CH_2)_{10}OH$.—Equivalent quantities of undecylamine hydrochloride dissolved in alcohol and sodium nitrite dissolved in water, were mixed together. A white precipitate was immediately deposited, which, when filtered off and dried, was found to decompose at 60° with evolution of gas. To obtain the alcohol the amine hydrochloride and sodium nitrite in solution in water were allowed to boil gently until gas ceased to be generated, care being taken to keep the solution neutral by adding a few drops of hydrochloric acid whenever a test showed it to be alkaline.

The oil formed was taken up by ether, and the solution dried by solid potassic hydrate. After removing the ether, the oil was distilled at reduced pressure. Four fractions were collected, about one-fourth of the product boiling at 84°–90°; a small quantity at 90°–118°; about one-third at 118°–126°, and the remainder about 126°. Upon redistilling the third fraction, the greater portion of it boiled at 123°. This boiling-point is lower than that expected for an alcohol occupying such a place in the series, and analysis showed it to be still impure.

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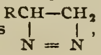
[1] Ann. Chem. (Liebig), **162**, 3.

[2] The formation of a derivative of a dialkylamine in this reaction points to the intermediate formation of a diazo body $RCH(N_2)$ which could alkylate a second molecule of the amine as easily as diazomethane methylates. The same diazo body would give with water the primary alcohol. The formation of a hydrocarbon $RCH{=}CH_2$, and particularly of a secondary alcohol, $RCHOHCH_3$, from a primary amine, points to isomeric diazo-bodies , whose discovery and investigation will probably be only a question of time. J. STIEGLITZ.

I. 0.3866 gram gave 1.025 gram CO_2, and 0.4440 gram H_2O.

II. 0.1928 gram gave 0.5198 gram CO_2, and 0.223 gram H_2O.

	Calculated for $C_{11}H_{23}OH$	Found. I.	II.
C	76.74	72.3	73.52
H	13.96	12.76	12.79

While the above figures are low for undecyl alcohol, yet they show that the body can be nothing but the alcohol in an impure condition. The alcohol was then further purified by converting it into undecylphenylurethane, which being a solid can be recrystallized until it gives a constant melting-point. By saponification the urethane yields the undecyl alcohol free from the hydrocarbon (see below) accompanying it, by the above method of preparation. The urethane also furnishes an excellent means of identifying the alcohol.

Normal Undecyl Phenylcarbamate, $C_6H_5NHCO_2C_{11}H_{23}$.—Six grams of the crude undecyl alcohol and 4.1 grams of phenyl isocyanate were mixed together in a flask and allowed to remain in a desiccator over night. The compound formed was dissolved in ligroin to remove any diphenylurea that might be present. After filtering, distilling off the ligroin, and recrystallizing from alcohol a number of times, a substance was obtained showing the constant melting-point 62° and crystallizing in needles.

0.2852 gram gave 12.9 cc. nitrogen at 755.7 mm. and 22°.

	Calculated for $C_6H_5NHCO_2C_{11}H_{23}$.	Found.
N	4.81	5.10

In order to convert undecylphenylurethane back into the alcohol, it was boiled for two hours with alcoholic potash. The solution was then poured into dilute acid, the oil taken up by ether, and the ether solution thoroughly washed with water, then dried for twenty-four hours with freshly-heated potassium carbonate. The alcohol remaining after removing the ether was then distilled under reduced pressure. The body when purified as described boiled at 131°, at 15° mm. pressure, and melted at 19°. Although both boiling-point and melting-point are those expected for undecyl alcohol, the figures obtained in analyzing the body were still a little low, showing a slight impurity.

0.2466 gram gave 0.6828 gram CO_2, and 0.2964 gram H_2O.

	Calculated for $C_{11}H_{23}OH$.	Found.
C	76.74	75.51
H	13.95	13.35

In order to determine whether the alcohol obtained was the primary or secondary (see above), it was oxidized by taking one part of the alcohol, two of potassium bichromate, three of sulphuric acid and nine of water, and boiling the mixture gently under an inverted condenser for twenty hours. The resulting product was extracted with ether, and the ether extract washed with water. After removing the ether by distillation, the residue was dissolved in alcohol and when the flask containing the solution was placed in a freezing-mixture, white crystals were formed. The crystals were filtered in a funnel surrounded by a freezing-mixture. The body had an acid reaction, and melted at 26°.

The silver salt was prepared by suspending the acid in water, neutralizing with ammonia and adding an excess of silver nitrate. The salt was washed, first with water, then with a small quantity of alcohol.

0.1602 gram gave 0.0577 gram silver.

	Calculated for $C_{11}H_{21}O_2Ag$.	Found.
Ag	36.86	36.01

The analysis of the silver salt, as well as the melting-point (26°), shows the oxidation product to be normal undecylic acid (m. p. 28.5°); consequently the substance from which it was obtained, must have been the hitherto unknown primary normal undecyl alcohol.

Undecylene, $CH_3(CH_2)_8CH : CH_2$.—The fraction boiling below 90°, which was obtained by distilling the product formed by the action of sodium nitrite on undecylamine hydrochloride, was redistilled. The greater portion of the product boiled at 84° at 18 mm. pressure.

0.1754 gram gave 0.5394 gram CO_2, and 0.225 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.71	83.86
H	14.28	14.25

As the analysis showed that the substance was not quite pure, it was converted into the dibromide, the boiling-point of which is so much higher than that of any of the other products that might be present, that there could be no difficulty in separating it from them by distillation.

Undecylene Dibromide, $CH_3(CH_2)_8CHBrCH_2Br$.—The undecylene (b.p. 84°, 18 mm.) was cooled in a freezing-mixture, and the calculated amount of bromine diluted by three and a half times its volume of carbon disulphide, added drop by drop. After removing the carbon disulphide, the heavy oil was distilled at reduced pressure. At 18 mm. it showed the constant boiling-point 161°.

A bromine determination by the Carius method gave the following results:

0.2068 gram substance gave 0.2490 gram AgBr.

	Calculated for $C_{11}H_{22}Br_2$.	Found.
Br	50.95	51.23

Nothing further was done with the second and fourth fractions excepting that a test showed the fourth fraction to be rich in nitrogen, the principal object of the study of the reaction being to determine whether the method could be used for preparing undecyl alcohol. Although undecyl alcohol is formed according to the equation,

$$C_{11}H_{23}NH_3Cl + NaONO = C_{11}H_{23}OH + N_2 + NaCl + H_2O,$$

the method is not to be recommended, as the yield obtained is very small, and it is very difficult to separate the alcohol from the other products of the reaction.

Preparation of Urethanes Directly from Acid Amides Dissolved in Ethyl Alcohol.

The yield of urethanes obtained by treating an acid amide dissolved in ethyl alcohol with sodium ethylate and bromine, is somewhat lower than that obtained when methyl alcohol is used as the solvent, yet, in every case in which the method has been tried, it is much higher than that obtained by the older method.

Ethyl Phenylcarbamate, $C_6H_5NHCO_2C_2H_5$.—The yield of ethylphenylurethane obtained by Swartz by treating dry benzbromamide with sodium ethylate was only 15 per cent of the theoretical, the remainder of the product being phenylbenzoylurea and unchanged amide. By proceeding in the following manner, a yield corresponding to 70 per cent of the theoretical was obtained.

5.7 grams (3 atoms) of sodium were dissolved in 142 grams of ethyl alcohol and the solution poured into a mixture of 10 grams (1 mol.) of benzamide, dissolved in 85 grams of ethyl alcohol, and 19 grams (1½ mols.) of bromine. The mixture was boiled for a few minutes on the water-bath, the alcohol distilled and the residue washed with water. After the product was thoroughly dried on a clay plate, it was distilled at reduced pressure. 9.6 grams of pure ethylphenylurethane were obtained, melting at 52°.

Ethyl-m-Nitrophenylcarbamate, $m\text{-}NO_2C_6H_4NHCO_2C_2H_5$.—By the older method Swartz obtained 6 per cent of ethyl-*m*-nitrophenylurethane and 53 per cent of nitrobenzoylphenylurea. By proceeding as in the last case 56 per cent of urethane was obtained with a considerable quantity of unchanged amide, but no urea.

Ethyl Pentadecylcarbamate, $C_{15}H_{31}NHCO_2C_2H_5$.—2.7 grams (3 atoms) of sodium, dissolved in 65 grams of ethyl alcohol, were poured into a mixture of 9.3 grams (1½ mols.) of bromine and 10 grams (1 mol.) of palmitic amide, dissolved in 40 grams of ethyl alcohol. After heating the mixture for a few minutes on the water-bath, a few drops of acetic acid were added and the alcohol distilled. The residue was washed with water, dissolved in ligroin and the undissolved portion filtered off. After removing the ligroin, the substance was distilled at 14 mm. pressure. It boils at 225° (14 mm.), and melts at 54°. It corresponds in every respect with the urethane obtained by me synthetically. The yield is 50 per cent of the calculated.

0.4838 gram at 749.5 mm. and 16° gave 21 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCOOC_2H_5$.	Found.
N	4.68	4.99

As in so many cases ureas were formed with such remarkable ease in the presence of alcohol (see undecyllaurylurea), some experiments were tried in order to find out whether they could be obtained by the direct action of an isocyanate upon an amide in alcoholic solution.

1. To a mixture of 1 gram (1 mol.) of benzamide, dissolved in 8 grams of methyl alcohol, 1 gram (1 mol.) of phenyl isocyanate was added, and the mixture heated for about five minutes on the water-bath. The products obtained, when purified, were identified as unchanged amide and phenylmethylurethane.

2. To 1 gram of benzamide in a 10 per cent caustic potash solution, 1 gram of phenyl isocyanate was added, and the mixture shaken up until the odor of isocyanate disappeared. The products obtained were diphenylurea (m. p. 235°) and unchanged amide.

3. 1.3 grams (1 mol.) of phenylurea chloride was added to 1 gram (1 mol.) of benzamide, dissolved in 12 grams of methyl alcohol, and the mixture heated for a few minutes on the water-bath. The odor of benzoic ether was quite noticeable, the other products obtained being ammonium chloride and phenylmethylurethane.

4. To a mixture of 1 gram (1 mol.) of benzamide, dissolved in 4 grams of methyl alcohol and 0.3 gram of sodium dissolved in 8 grams of methyl alcohol, 1.3 grams (1 mol.) of phenylurea chloride were added. The products obtained were benzamide and methylphenylurethane.

As not the slightest trace of phenylbenzoylurea was obtained in any of the above experiments, it is quite evident that an isocyanate, in its ordinary condition, does not act upon an amide as readily as upon an alcohol.

Action of Sodium Methylate and Bromine on Cinnamic Amide.

To a mixture of 8 grams of cinnamic amide dissolved in 45 grams of methyl alcohol, and 2.7 grams (2 atoms) of sodium, dissolved in 70 grams of methyl alcohol, 8.7 grams of bromine were added in small portions at a time. The mixture was heated for a short time on the water-bath, and after adding a few drops of acetic acid, the alcohol was allowed to evaporate spontaneously. The product remaining was shaken up with ether. A portion dissolved, but a considerable quantity remained undissolved. The undissolved portion was washed with water to remove the sodium bromide, and for analysis it was recrystallized two or three times from alcohol. The body melts at 218° with decomposition.

I. 0.1566 gram gave 7.5 cc. nitrogen at 747.5 mm. and 16°.

II. 0.1402 gram gave 0.2358 gram of CO_2, and 0.0618 gram H_2O.

	Calculated for $C_{10}H_{12}NO_2Br$.	Found.
C	46.51	45.86
H	4.65	4.89
N	5.42	5.49

The presence of considerable bromine in the compound was proved by a qualitative test. No rearrangement had taken place, as the body, when heated with a solution of caustic potash, gave off ammonia, showing that the amido group had remained unchanged. No effort was made to determine the constitution of the body, but in all probability the constitutional formula is $C_6H_5CHBrCH(OCH_3)CONH_2$, or possibly with the bromine and methoxy group exchanged.

From the ether solution a thick pasty substance was obtained which could not, by any means employed, be crystallized, and as it decomposed when distilled *in vacuo*, it was not obtained sufficiently pure for analysis.

Action of Sodium Methylate and Bromine upon Salicylic Amide.

McCoy[1] in treating salicylic amide with bromine and alkali in solution in water according to Hofmann's reaction, found that the benzene ring is brominated twice before the rearrangement is effected. The same reaction when tried by me in methyl alcohol, gave the same result. The experiment was carried out as follows:

To a mixture of 10 grams (1 mol.) of salicylic amide, dissolved in 66 grams of methyl alcohol and 5 grams (3 atoms) of sodium, dissolved in 110 grams of methyl alcohol, 11.6 grams (1 mol.) of bromine were added. The product obtained was identified as dibromsalicylic amide melting at 183°.

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[1] This JOURNAL, 21, 116.

It is evident that the method of preparing urethanes, described in this paper, cannot on account of the reactivity of the reagents, be used to effect a rearrangement of bodies analogous to salicylic or cinnamic amide. In such cases the method of Curtius[1] is the most satisfactory.

The results of the work described in this paper and the conclusions to be drawn from them can be briefly summarized as follows:

1. Urethanes are obtained without the isolation of the brom- or chloramides by the action of a sodium alcoholate on a mixture of an acid amide and bromine.

The method is applicable to the preparation of both aromatic and aliphatic urethanes, in ethyl and methyl alcohol solution, but cannot be used when the acid amide is unsaturated or otherwise very susceptible to bromine.

2. The urethanes, when distilled with slaked lime, give amines quantitatively according to

$$RNHCOOCH_3 + Ca(OH)_2 = RNH_2 + CaCO_3 + HOCH_3.$$

As the urethanes were also obtained in excellent yield, this method was found to be a practical one for the preparation of higher aliphatic amines.

3. The amines, obtained by the above-described method, are primary monoalkylamines as shown: (*a*) by the preparation of a mustard oil and an isocyanate from pentadecylamine; (*b*) by the formation of primary alcohols when sodium nitrite was allowed to act upon the amine hydrochlorides.

4. The formation of acyl alkylureas in applying the Hofmann reaction in aqueous or alcoholic solution takes place whenever, owing to the slowness of the reaction, considerable unchanged acid amide is present, while the remainder of the acid amide is suffering "rearrangement"; the rearranged portion then acts upon the unchanged amide even in the presence of alcohol or water and forms a urea.

5. Experiments show that an isocyanate in its ordinary condition, will not act upon an acid amide in the presence of alcohol or water.

I wish here to express my sincere thanks to Professor Stieglitz, who directed and advised me in this work.

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[1] J. prakt. Chem., **52**, 227, 433.

Contributions from the Chemical Laboratory of Harvard College.

CXIII.—AN ELECTRIC DRYING OVEN.

By Theodore William Richards.

Practical chemists have long sought for an ideal drying oven. The qualities which should be possessed by this piece of apparatus are the following: cleanliness, durability, ease of regulation, constancy, and cheapness. Porcelain and glass are the only materials, except platinum, which commend themselves to the accurate experimenter as far as cleanliness is concerned; but these substances are so easily cracked by rapidly changing temperature that some ignoble metal is usually chosen, with the well-known untidy results. If illuminating gas is used as the source of heat, the products of combustion should be carefully excluded from the interior of the oven, because of the sulphurous oxide which is present; hence a large part of the heat is usually wasted.

The commercial use of electricity as a heating agent is well known to all, and the difficulties referred to above can be so readily overcome by its assistance, that an electric drying oven for chemists cannot be a new thing. Nevertheless, since such a piece of apparatus is not commonly known, perhaps the hints contained in this brief note may be useful to those who have not happened to think of the device.

An ordinary sixteen candle-power incandescent lamp gives heat enough to raise a small oven padded with asbestos to 120° or 130°. It may be arranged in the fashion sketched in the first figure, a large lamp-chimney serving as the lining of the oven, while the outside casing consists of a "tin" can with holes cut in the bottom and the lid. The crucible or funnel to be heated may be supported either from above or from below.

While simple contrivances of this kind may occasionally answer, the brilliant light shed by this source of heat is not permissible when some substances are to be dried; and, moreover, larger vessels must often be heated, and higher temperatures attained.

Obviously a great variety of resistances might be used for converting the electrical energy into heat, and with alternating currents ohmic resistance might be assisted by impedance and hysteresis. By suitable adjustment of current and other circumstances, any temperature between the temperature of the room and 3000° or more might be obtained; but the present description is concerned only with the easily obtained conditions necessary to operate a drying oven suited to the uses of the analytical chemist.

A coil of wire wrapped around a suitable insulator is perhaps the most convenient resistance for the present purpose, and while iron or German silver wire will serve for a short time, platinum is of course the best material. A platinum wire 0.2 mm. in diameter, exposed to warm air, is heated almost but not quite to redness by a current of two amperes; and, since two amperes may be safely taken from a circuit designed for electric lighting, this wire is a convenient size. Five meters of this wire, when thus heated, have a resistance of not far from twenty-five ohms,—the resistance needed if one has a fifty volt current at his disposal. The corresponding amount of energy (100 watts, or twice the amount taken by a sixteen candle-power lamp) is capable of heating an oven large enough for most of the needs of an analytical chemist. The form and thermal insulation of the oven have so much effect upon the result that the details must be largely a matter of trial; but these figures will enable anyone who has a slight knowledge of electricity to arrange a contrivance approximately suited to his own needs. For example, from the common 8 volt accumulator plant one must draw five or six amperes for a small oven, and two or three times that amount for a large one; a thin ribbon of platinum foil would probably form the best resistance with this large current. The oven should of course be adjusted to furnish the maximum temperature desired; for diminution of the current by the interposition of outside resistance, or admission of more air, enables one to lower this temperature to any degree.

The most serious difficulty which was encountered in the practical execution of the plan was the inequality of the temperatures observed in different parts of the bath, an inequality which may easily amount to as much as 30° or 40°. This

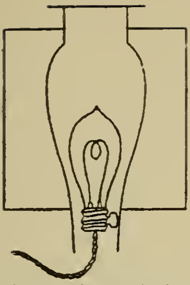

Fig. 1. Simple drying oven using an incandescent lamp as the source of heat.

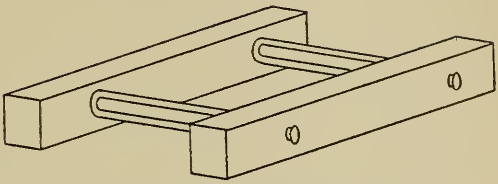

Fig. 2. Frame of porcelain and glass around which a platinum resistance may be wound.

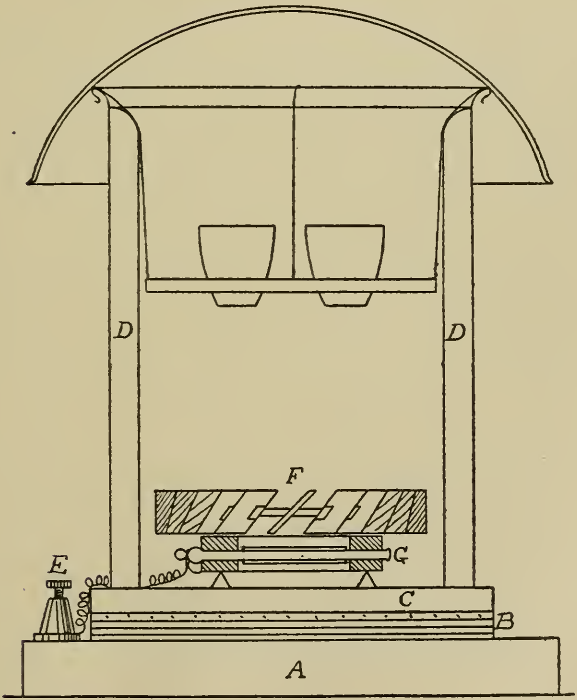

Fig. 3. Complete drying oven, vertical section. A=base; B=layers of asbestos to protect base; C=porcelain tile; D=annular space packed with non-conducting material; E=wire leading to resistance; F=stationary fan made of inclined mica vanes attached to platinum foil; G=section of frame shown in Fig. 2.

difficulty may be completely overcome by a stationary propeller-diaphragm placed directly over the coil of heated wire. The oblique vanes of this diaphragm produce a spirally ascending current which causes the air in the oven to mix in a very thorough manner, so that a thermometer near the walls gives a temperature within 2° of that registered by a thermometer in the center.

A brief description of the general problem having been given, the details of a simple but efficient air-bath built in accordance with these principles may not be out of place.

The base of the oven consists of a stout piece of hard wood 20 cm. square [A, Fig. 3.]. Upon it rest several alternate squares of ignited asbestos paper and wire gauze [B], and upon these rests a porcelain tile [C], which forms the bottom of the chamber. The walls of the oven are formed by a large beaker, 12 cm. in diameter, cut off horizontally near its base, and 20 cm. high. The annular space [D] between this beaker and a larger one encircling it, is partially filled with three or four layers of ignited asbestos paper, or with loosely packed asbestos wool, in order to prevent loss of heat. A large "clock" glass or, if darkness is needed, an inverted evaporating dish or a porcelain tile, forms the lid, which also should be provided with an asbestos covering. When access to the interior is desired the whole cylindrical wall may be raised, or merely the lid removed, according to the needs of the occasion.

Two binding-posts, screwed into the wood, serve to connect the apparatus with the source of energy (52 volts). Medium-sized platinum wires [E] lead the current beneath the broken edges of the beaker to the heat-producing resistance, which may be mounted in the base of the chamber upon one of a variety of insulators of porcelain, glass, or mica. A very convenient arrangement for this purpose consists of two of the ordinary porcelain clamps (8 cm. long) used for securing electric wires, held together by glass rods passed through their screw holes, and held apart by shorter glass tubes encircling the rods. Around the porcelain sides of this frame (which is shown in Fig. 2) are tightly wound the 5 meters of No. 32 (B. & S.) platinum wire (0.2 mm. in diameter and 3.4 grams in weight) the coils being laid at least 1.5 mm. apart to avoid accidental contact when the wire expands upon heating. In some cases plates of mica have been used to prevent this contact, but usually this precaution is unnecessary. The frame, with its resistance-wire, is supported half a centimeter above the base by means of pieces of pipe-stem or of glass; and above this, propped upon other bits of pipe-stem, or upon a glass stand, is placed the stationary screw-propeller [F] which agitates the ascending column of air. Obviously nothing is easier than to regulate the amount of air admitted by raising or lowering the cylindrical wall. The screw propeller may be made by simply cutting radial slits in a disk of tinned iron or platinum foil, and turning the segments to an angle of 45° with the plane of the disk; or it may be made of mica vanes attached to a platinum center, according to the purse and the taste of the user. The tinned iron disc will probably answer most purposes, for it is readily replaced when worn out.

The vessel to be heated may be supported by a tripod from below, or perhaps more neatly by a triangle or quadrangle suspended from above. By the judicious combination of pipe-stem or glass tube and platinum wire, a support may be made which is both strong and inexpensive. If platinum alone is used the wire must be stout and therefore costly. This oven gives a temperature 140° above that of the room in which it is placed, when no outside resistance is interposed.

It is needless to point out the great cleanliness, convenience, safety, and economy of this simple drying apparatus. The real test of such a device is to be found in its daily performance, and this is so satisfactory in constancy and in ease of accurate regulation at any desired point as to leave nothing to be desired. Large ovens for the use of classes have not yet been constructed, but probably no difficulty will be experienced in building permanent structures which will be a boon to students in quantitative analysis.

CXIV.—ON CERTAIN DERIVATIVES OF SYMMETRICAL TRICHLORBENZOL.[1]

By C. Loring Jackson and F. H. Gazzolo.

In a paper by Sidney Calvert and one of us,[2] the behavior of tribromiodbenzol, $Br_3 1,3,5,I2$, and of tetrabrombenzol, $Br_4 1,2,3,5$, with sodic ethylate was studied, and it was shown that the atom of iodine (or the atom of bromine in the corresponding position) was replaced by hydrogen under these conditions, giving the symmetrical tribrombenzol. It seemed of interest in this connection to study the corresponding trichlor compounds; that is, the trichloriodbenzol and the trichlorbrombenzol, to see whether the loosening effect of the three chlorine atoms might not be even greater than that of the three atoms of bromine, and thus make it possible that these substances would react with other agents besides sodic alcoholates, which were the only reagents that had any such effect upon the bromine compounds.

At that time it was not worth while to undertake the work, because of the great difficulty in preparing symmetrical trichloraniline, but since this obstacle has been removed by the beautiful method of Victor Meyer and Sudborough,[3] we have prepared these compounds and studied some of their relations. Trichloriodbenzol, $Cl_3 1,3,5,I2$, melts at 55°; and by treatment with sodic ethylate dissolved in alcohol and benzol, yielded symmetrical trichlorbenzol recognized by its melting-point 64° and two analyses. It therefore behaved like the tribromiodbenzol under these conditions. All our other attempts to obtain a simple replacement of the iodine in this substance failed, so that it is no more reactive than the tribromiodbenzol. Fuming nitric acid converted the trichloriodbenzol into the trichlordinitrobenzol melting at 129°, iodine being set free.

The trichlorbrombenzol, $Cl_3 1,3,5,Br2$, melts at 65°; that is, at nearly the same temperature as the symmetrical trichlorbenzol 63°.4 (Körner), and what is strange, higher than the corresponding trichloriodbenzol. With sodic ethylate it lost bromine, but the reaction was not specially studied. When treated with fuming nitric acid it gave a trichlorbromdinitrobenzol melting at 175°, which was a decidedly reactive substance. Aniline replaced the three atoms of chlorine, giving the trianilidobromdinitrobenzol, $C_6(C_6H_5NH)_3Br(NO_2)_2$, melting at 175°–176°, discovered by W. D. Bancroft and one of us.[1]

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[1] Presented to the American Academy of Arts and Sciences, October 12, 1898.

[2] This Journal, **18**, 298.

[3] Ber. d. chem. Ges., **27**, 3151.

Sodic ethylate also acts upon it, probably giving a number of products, to judge from analogy and the fact that both sodic bromide and sodic nitrite were detected among them, but we have only succeeded in identifying one of these with certainty; this is a bromdinitroresorcine diethylether melting at 81°–82°, and probably having the following constitution, $(OC_2H_5)_2 1,3, Br 2 (NO_2)_2 4,6$, although it may be that one of the ethoxy groups stands at 5 instead of 3. It must have been formed by the replacement of two atoms of chlorine by two ethoxy groups, and the third by hydrogen. As in most of the replacements of a halogen by hydrogen it has been found that it stood between two nitro groups, we think there can be little doubt that the first constitution assigned to this body is the correct one. Its formation is interesting, as it is the first case we have found in which chlorine has been replaced by hydrogen under these conditions. In all the other cases studied the chlorine has remained unaltered or has entered into some simple reaction: thus picryl chloride gave picryl ether,[2] picryl malonic ester,[3] or picryl acetacetic ester,[4] according to the reagent used; chloranil gave dichlorquinonedimalonic ester;[5] or, so far as the replacement alone was concerned, dichlordiethoxyquinone,[6] and trichlordinitrobenzol gave dichlordinitrophenylmalonic ester,[7] or chlordinitroresorcine diethylether, and dinitrophloroglucine triethylether.[8] These last cases are especially striking, since the corresponding tribromdinitrobenzol showed a replacement of bromine by hydrogen, when treated with sodium malonic ester or sodic ethylate.

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[1] This JOURNAL, **12**, 294.

[2] Jackson and Boos: *Ibid.*, **20**, 444.

[3] Jackson and Soch: *Ibid.*, **18**, 133.

[4] Dittrich: Ber. d. chem. Ges., **23**, 2720.

[5] Stieglitz: This JOURNAL, **13**, 38.

[6] Kehrmann: J. prakt. Chem. [2], **40**, 367; Jackson and Grindley: This JOURNAL, **17**, 602.

[7] Jackson and Lamar: This JOURNAL, **18**, 775.

[8] Jackson and Lamar: *Ibid.*, p. 668.

This bromdinitroresorcine diethylether, melting at 81°-82°,

$$(OC_2H_5)_2 1,3,Br2,(NO_2)_2 4,6?$$

is isomeric with that melting at 184°,

$$(OC_2H_5)_2 1,5,Br3,(NO_2)_2 2,4,$$

and that melting at 92°,

$$(OC_2H_5)_2 1,3,Br5,(NO_2)_2 2,4,$$

made by the action of sodic ethylate on the symmetrical tribromdinitrobenzol.

The trichlorbromdinitrobenzol also reacted with sodium malonic ester, but we were unable to bring the product into a state fit for analysis. When the dry substance was treated with sodic ethylate, it gave a deep vermilion product, which probably belongs to the class of colored compounds formed by sodic ethylate and certain nitro bodies,[1] as it was decomposed by water and some organic solvents. This is the first case, so far as we can find, in which one of these substances has been observed derived from a compound of benzol with all its atoms of hydrogen replaced by other radicals.

Trichloriodbenzol, $C_6H_2Cl_3I$.

To prepare this substance 17 grams of sublimed trichloraniline (made by the excellent method of V. Meyer and Sudborough[2]) were mixed with moderately dilute sulphuric acid in the proportion of 1 molecule of trichloraniline to each molecule of sulphuric acid, and after thorough cooling powdered sodic nitrite was added in small successive quantities, until the nitrous fumes generated were no longer absorbed. After each addition of the sodic nitrite the flask was corked and vigorously shaken, until all the red fumes were absorbed, care being taken that the contents were kept cool throughout the operation. When a sufficient amount of sodic nitrite had been added, the mixture was filtered, the cooled filtrate freed as completely as possible from the excess of nitrous fumes by vigorous shaking, and then treated with a distilled aqueous solution of hydriodic acid, until there was no further action.

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[1] This JOURNAL, **19**, 199, where a complete list of the papers on this subject is given.

[2] Ber. d. chem. Ges., **27**, 3151.

The brownish precipitate thus obtained was washed, first with a solution of potassic iodide to remove free iodine, and finally with water, after which it was purified by sublimation, or by crystallization from hot alcohol, until it showed the constant melting-point 55°. It was dried *in vacuo*, and gave the following results on analysis :

0.2188 gram of the substance gave, by the method of Carius, 0.4746 gram of a mixture of argentic chloride and iodide. After washing this precipitate with ammonic hydrate, 0.1672 gram of argentic iodide was left undissolved.

	Calculated for $C_6H_2Cl_3I$.	Found.
Cl and I	75.94	76.10
Cl	34.69	34.73
I	41.30	41.29

The substance is therefore trichloriodbenzol, and as it was made from ordinary trichloraniline its constitution must be $Cl_3$1,3,5,I2.

Properties of Trichloriodbenzol.—It crystallizes from alcohol in white, slender needles terminated by one plane at a very acute angle ; these needles are often a centimeter or more long, and are much branched, the branches forming a sharp angle with each other and developing into forms like feathers. It melts at 55° and sublimes easily. It is freely soluble in ether, benzol, chloroform, acetone, carbonic disulphide, or ligroin ; soluble in ethyl or methyl alcohol, when cold, more freely soluble when hot ; soluble in glacial acetic acid ; insoluble in water, cold or hot. A mixture of alcohol and chloroform is the best solvent for it. It is apparently unaffected by the strong acids, or by sodic, potassic, or ammonic hydrate.

Behavior of Trichloriodbenzol with Sodic Ethylate.

Two grams of trichloriodbenzol dissolved in anhydrous benzol were mixed with 20 cc. of an alcoholic solution of sodic ethylate made from 1 gram of sodium, and the mixture was allowed to stand over night. The liquid turned dark brown, and a precipitate began to separate soon after adding the ethylate. To make certain that the reaction was complete, the mixture was heated on the steam-bath in a flask with a return condenser, which rendered the brown color much darker. The product was then evaporated to dryness. During the evaporation an odor like that of an aldehyde was observed, but the presence of one could not be determined by other tests. The dry residue was treated with water, and the insoluble portion separated from the solution, which gave tests for an iodide. The portion insoluble in water, which was very dark brown, was washed thoroughly, and then purified by crystallization from alcohol, until it showed the constant melting-point, 64°, which proved that it was the symmetrical trichlorbenzol. This was confirmed by the following analyses of the substance dried *in vacuo* :

I. 0.0906 gram of the substance gave, by the method of Carius, 0.2154 gram of argentic chloride.

II. 0.0792 gram of the substance gave 0.1862 gram of argentic chloride.

	Calculated for $C_6H_3Cl_3$.	Found. I.	II.
Cl	58.68	58.78	58.13

Behavior of Trichloriodbenzol with Other Reagents.

With aniline even at its boiling-point trichloriodbenzol showed no signs of action, except that the color of the mixture became darker, and a certain amount of turbidity appeared, but no test for an iodide could be obtained, and the trichloriodbenzol was recovered unaltered.

When trichloriodbenzol was heated on the steam-bath for three hours with an aqueous solution of sodic hydrate, the liquid took on a chrome-yellow color, but this must have been due to a very slight reaction, as after acidification it gave no precipitate with argentic nitrate, and essentially the whole of the trichloriodbenzol was recovered unaltered.

Melted sodic hydrate, on the other hand, seemed to act upon it, as a brownish mass was obtained, which after solution in water gave a slight precipitate on acidification and a reddish solution ; a good test for an iodide was obtained, but the yield of the new organic substance was so small that we did not study this reaction further, since at best it seemed to us of slight interest.

Sodium malonic ester had little or no action on the trichloriodbenzol, most of which was recovered unaltered from the product, so that the hope of obtaining enough of a substance (if one were really formed) for analysis was so small that we did not continue work in this line.

From these experiments it appears that the trichloriodbenzol is no more reactive than the tribromiodbenzol, from which exactly similar results were obtained by Sidney Calvert and one of us.[1]

When trichloriodbenzol was mixed with nitric acid of specific gravity 1.50 and strong sulphuric acid, and the mixture gently heated, the solid went into solution. It was allowed to stand at the ordinary temperature over night, and then precipitated with a large quantity of water, when a mixture of a white body and scales of iodine was thrown down. The iodine was recognized by its crystalline form, color, smell, and purple fumes. The white body was purified by crystallization from alcohol, when it showed the melting-point 129°, and is therefore the trichlordinitrobenzol, $Cl_3 1,3,5, (NO_2)_2 2, 4$.

Trichlorbrombenzol, $C_6H_2Cl_3Br$.

Twenty grams of trichloraniline dissolved in 100 cc. of hot glacial acetic acid were mixed with 90 cc. of hydrobromic acid (boiling at 125°), and, disregarding the heavy, grayish-yellow precipitate, the mixture was thoroughly cooled in an ice-bath, and then treated with powdered sodic nitrite, until red fumes were given off freely. The sodic nitrite was added in small quantities at a time, and the flask containing the mixture shaken vigorously after each addition, the liquid being kept cool throughout. The heavy precipitate already mentioned went into solution during the addition of the sodic nitrite, forming a dirty yellow liquid. After standing for a few hours to complete the reaction, the contents of the flask were poured into an evaporating-dish, and heated for an hour on the steam-bath. In this way a dark oily product floating on the surface of the liquid was obtained, which solidified on cooling. The mother-liquor deposited more of this product in a semicrystalline condition, and an additional amount was obtained from it by heating it again with more hydrobromic acid. The product was purified by sublimation, followed by recrystallization from alcohol, until it showed the constant melting-point, 64°–65°. As this is the same as the melting-point of trichlorbenzol, we supposed at first that our product was this body, but the following analyses of the substance dried *in vacuo* showed that it was the desired trichlorbrombenzol.

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[1] This JOURNAL, 18, 304.

I. 0.1618 gram of the substance gave, by the method of Carius, 0.3850 gram of the mixture of argentic chloride and bromide.

II. 0.1116 gram of the substance gave 0.2656 gram of the mixture of argentic chloride and bromide.

III. 0.1276 gram of the substance gave on combustion 0.1274 gram of carbonic dioxide and 0.0108 gram of water.

	Calculated for $C_6H_2Cl_3Br$.	Found.		
		I.	II.	III.
Cl and Br[1]	71.60	71.76	71.74	....
C	27.64	....	....	27.23
H	0.77	....	....	0.94

The yield of trichlorbrombenzol was 12 grams, instead of the 26.5 grams which should have been obtained from 20 grams of trichloraniline, that is, over 45 per cent of the calculated quantity.

Properties of Trichlorbrombenzol.—It crystallizes from alcohol in white radiating needles, which develop into long, slender, blunt-ended prisms. It melts at 64°–65°; that is, one degree higher than the symmetrical trichlorbenzol, which melts, according to Körner, at 63°.4; not only is this coincidence striking, but it is also surprising that it should melt at a higher temperature than the trichloriodbenzol, which melts at 55°. It sublimes easily. It is freely soluble in ether, benzol, or acetone; soluble in cold alcohol, more freely in hot; soluble in glacial acetic acid, or ligroin; less soluble in methyl alcohol, and still less in carbonic disulphide. The best solvent for it is alcohol. The three strong acids have no apparent action on it, but fuming nitric acid converts it into trichlorbromdinitrobenzol, as described later. When a benzol solution of the trichlorbrombenzol was treated with sodic ethylate, the atom of bromine was removed, as was shown by testing the wash-waters from the product for bromine, when a strong reaction for it was observed.

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[1] By a curious coincidence the results of analyses I and II, if calculated as argentic chloride, give numbers agreeing excellently with the percentages calculated for $C_6H_3Cl_3$, so that the combustion was necessary to determine whether our compound was this, or the $C_6H_2Cl_3Br$, which has the same melting-point.

Trichlorbromdinitrobenzol, $C_6Cl_3Br(NO_2)_2$.

To prepare this substance the trichlorbrombenzol was mixed with nitric acid of specific gravity 1.52, and one-third the quantity of strong sulphuric acid, and the mixture heated gently for an hour. At first the solid dissolved, but later the nitro compound was deposited from the solution. After the mixture had stood over night, the supernatant acid was poured into a large quantity of water, which gave an additional amount of the product. It was purified by crystallization from a mixture of alcohol and benzol until it showed the constant melting-point, 175°, when it was dried *in vacuo*, and analyzed with the following result :

0.1654 gram of the substance gave, according to the method of Carius, 0.2914 gram of the mixture of argentic chloride and bromide.

	Calculated for $C_6Cl_3Br(NO_2)_2$.	Found.
Br and Cl	53.21	53.10

The constitution of this substance is settled by the method by which it was made as $Cl_3 1,3,5, Br 2, (NO_2)_2 4,6$. The yield is essentially quantitative.

Properties of Trichlorbromdinitrobenzol.—It forms, when crystallized from alcohol and benzol, thick, rather blunt, rhombic plates, the obtuse angles of which are frequently beveled by two planes. They show a tendency to form groups with the members superimposed, and have a slight yellowish tinge. The substance melts at 175°, and is very soluble in chloroform, acetone, or carbonic disulphide ; slightly soluble in ethyl or methyl alcohol, either cold or hot ; insoluble in cold, soluble in hot glacial acetic acid; essentially insoluble in ligroin, or in hot or cold water. The best solvent for it is a mixture of benzol and alcohol. Strong hydrochloric or sulphuric acid has no apparent action on it. Fuming nitric acid dissolves it when hot. It sublimes easily, and in this way feathery, ivory-white crystals are obtained sometimes over a centimeter in length.

Action of Aniline on Trichlorbromdinitrobenzol.

When one gram of trichlorbromdinitrobenzol was warmed gently with a slight excess of freshly-distilled aniline it went into solution, forming a cherry-red liquid, the color of which became deeper on longer heating. To obtain the product the liquid was poured into a large quantity of water, acidified with hydrochloric acid, and the crimson precipitate formed in this way thoroughly washed and crystallized from a mixture of alcohol and benzol until it reached the constant melting-point, 175°–176°. This showed that the substance was the bromdinitrotrianilidobenzol, $C_6Br(NO_2)_2(C_6H_5NH)_3$, obtained by W. D. Bancroft and one of us[1] from tetrabromdinitrobenzol and aniline. In this case it was formed by the replacement of the three atoms of chlorine by three anilido groups.

Behavior of Trichlorbromdinitrobenzol with Sodic Ethylate in the Cold.

Five grams of trichlorbromdinitrobenzol dissolved in anhydrous benzol were mixed with the sodic ethylate made from 25 grams of absolute alcohol and 1 gram of sodium, which gave the proportion of 3 molecules of the ethylate to each molecule of trichlorbromdinitrobenzol. The two substances reacted at once, since the liquid took on a bright scarlet color as soon as they were mixed, and there was also a slight evolution of heat. To complete the reaction the mixture was allowed to stand three days at ordinary temperatures, during which time a heavy precipitate was deposited, and the color changed to a yellowish-red. The precipitate was filtered out, washed with alcohol, and then dissolved in water. This solution gave a strong test for sodic nitrite with potassic iodide, starch paste, and dilute sulphuric acid, and also a heavy white precipitate with argentic nitrate and nitric acid. To obtain the organic products of the reaction the reddish alcoholic filtrate was allowed to evaporate spontaneously, and the residue treated with water; the insoluble substance thus obtained was purified by crystallization from alcohol until it showed the constant melting-point, 81°–82°, when it was dried *in vacuo*, and analyzed with the following result:

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[1] This JOURNAL, **12**, 294.

I. 0.1236 gram of the substance gave, by the method of Carius, 0.0684 gram of argentic bromide.

II. 0.2500 gram of the substance gave 18.4 cc. of nitrogen at a temperature of 23° and a pressure of 754.7 mm.

	Calculated for $C_6HBr(C_2H_5O)_2(NO_2)_2$.	Found. I.	II.
Br	23.89	23.56	....
N	8.36	....	8.24

The substance is therefore a bromdinitroresorcine diethylether formed from the trichlorbromdinitrobenzol by the replacement of two atoms of chlorine by ethoxy groups, and of the third by hydrogen. Certain points in regard to its constitution are settled, since the two ethoxy groups must be in the meta position to each other, and the atom of bromine and the two nitro groups are in the symmetrical position to each other. The radicals therefore are probably arranged as follows:

$$(C_2H_5O)_21,3,Br2,(NO_2)_24,6\,;$$

but it is possible that one of the ethoxy groups instead of the atom of hydrogen, stands at 5 between the two nitro groups. It is isomeric with the bromdinitroresorcine diethylether melting at 184°, and made by Warren and one of us[1] from tribromdinitrobenzol and sodic ethylate in the cold, which has the constitution $(C_2H_5O)_21,5,Br3,(NO_2)_22,4$, and also with that melting at 92° obtained by Koch and one of us,[2] as another product from the same reaction, which has the constitution

$$(C_2H_5O)_21,3,Br5,(NO_2)_22,4.$$

The yield of the bromdinitroresorcine diethylether was 1 gram from 5 of the trichlorbromdinitrobenzol; that is, about 21 per cent of the theoretical yield.

Properties of Bromdinitroresorcine Diethylether, melting at 81°–82°, $C_6H(C_2H_5O)_2Br(NO_2)_2$.

It forms, when crystallized from alcohol, white needles or slender prisms terminated by two planes at an obtuse angle to each other, which turn brown on exposure to the light. It melts at 81°–82°, and is very soluble in benzol, or chloroform; soluble in methyl alcohol, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold ethyl alcohol, more soluble in hot; slightly soluble in ligroin. Alcohol is the best solvent for it. It is not acted on apparently by strong hydrochloric acid, either hot or cold; strong sulphuric acid does not act in the cold, but when warm dissolves it with a brownish red color; strong nitric acid does not act in the cold but gives a colorless solution with it when hot.

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[1] This JOURNAL, **13**, 167.

[2] *Ibid.*, **21**, 510.

That this bromdinitroresorcine diethylether was not the only organic product of the reaction of sodic ethylate on trichlorbromdinitrobenzol was shown by the fact that sodic nitrite as well as sodic chloride was formed. Our attempts to isolate these other bodies, however, were far from successful. Some experiments with the aqueous wash-waters seemed to indicate that they contained a phenol melting at 111°, and having perhaps the formula $C_6(OC_2H_5)_2OH(NO_2)_2Br$, but the analytical data obtained were too imperfect to justify a description of the body; and we did not succeed in bringing any of the other products into a state fit for analysis.

The trichlorbromdinitrobenzol seemed to give colored compounds with sodic ethylate similar to those given by picryl chloride and several other nitro compounds, since upon adding an alcoholic solution of sodic ethylate to the dry substance it took on a strong vermilion color, which was instantly destroyed by water, and more slowly by benzol or ligroin. The fact that the color disappeared on the addition of water indicates that it is one of the colored compounds under discussion, and not a salt of a phenol. Another sample of the substance was allowed to stand for half an hour exposed to the air, at the end of which time the red color had given place to yellow. As the colored compound was less stable than several others which have been studied, its investigation was not carried further.

The trichlorbromdinitrobenzol is acted on by an alcoholic solution of sodium malonic ester. Our first experiments gave a crystalline product, but in too small quantity for analysis. Our later experiments have yielded only viscous masses, from which we have not succeeded in obtaining anything for analysis in spite of a very large expenditure of time and material.

NARCOTINE AND NARCEINE.

BY GEORGE BELL FRANKFORTER AND FRANK H. KELLER.

In 1888, Roser, in an important paper on narcotine, obtained from narcotine-methyl iodide by a complex process, a base which closely resembled the alkaloid narceine both in physical and chemical properties. Owing to the apparent difference of 1 molecule of water, the substance was called pseudonarceine. Its formation can be represented by the following equation:

$$C_{22}H_{22}NO_7 + CH_3I = C_{23}H_{26}NO_7I.$$

By converting the above iodide into the chloride and treating with an alkali, the chlorine was replaced by the hydroxyl group, forming narcotine-methyl hydroxide:

$$C_{23}H_{26}NO_7I + NaOH = C_{23}H_{26}NO_7OH + NaI.$$

This narcotine-methyl hydroxide, when warmed by passing steam into the solution, or allowing to stand for some time, changes into the so-called pseudonarceine.

While these reactions appear comparatively simple, what actually takes place in the above treatment is quite the opposite. Besides this base, which has since been identified as narceine, a second substance is formed, which was identified by Roser as dimethyltoluene azammonium silver iodide,

$$C_7H_6(CH_3)_2N_3I.2AgI.^2$$

This strange reaction led to a careful examination of the above substance. While in general it does resemble the azimido compounds of Zincke and Lawson, a number of analyses were made without obtaining satisfactory results. A careful comparison of the two substances showed that they were similar, in so far as they were insoluble in nearly all common solvents. The product of Zincke and Lawson was soluble in aniline, nitrobenzene, quinoline, and a strong solution of sodium hyposulphite, from which it was obtained in well-crystallized form. The substance from narcotine proved to be insoluble in cold nitrobenzene, but slightly soluble in

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[1] Ann. Chem. (Liebig), **247**, 167. [2] *Ibid.*, **240**, 128.

hot, changing color from a light gray to a light lemon-yellow. On cooling, the yellow color immediately disappeared and the substance was precipitated as an amorphous mass. There was no indication of the formation of a double salt when treated with aniline. In fact, this same yellow substance was obtained from nitrobenzene, aniline, and quinoline. The substance from narcotine melted at 184°–186° C. The compound of Zincke and Lawson melted at 128°–130° C. Neither substance contained water of crystallization.

Analyses of the substance from narcotine gave the following results:

I. 0.1937 gram substance gave 0.1279 gram CO_2, and 0.0316 gram H_2O.

II. 0.2162 gram substance gave 0.1413 gram CO_2, and 0.0345 gram H_2O.

III. 0.2112 gram substance gave 0.1364 gram CO_2, and 0.0333 gram H_2O.

IV. 0.2361 gram substance gave 0.1729 gram AgI.

V. 0.4016 gram substance gave 0.0235 gram N.

	Calculated for $C_7H_6(CH_3)_2N_3I.2AgI$.	Found.				
		I.	II.	III.	IV.	V.
C	14.23	18.00	17.82	17.61	....	....
H	1.58	1.8	1.77	1.75	....	....
N	5.53	....	....	....	....	4.99
I	50.20	....	....	....	39.54	....

The substance from which the above analyses were made was prepared at different times and purified by treating with absolute alcohol and ether. The wide difference between the calculated results and the results of the analyses make it doubtful if these two substances are identical. In fact, it is doubtful if the formula given by Zincke and Lawson[1] is correct as is indicated by the single analysis made by them. If this substance is an azimido compound, it probably contains both iodine and chlorine, one-third of the iodine having been replaced by chlorine. Such a formula agrees very much better with the analyses than does the formula above given.

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[1] Zincke and Lawson made one simple determination of silver iodide, obtaining 66.3 per cent. The theoretical is only 61.9.

	Calculated for	Found.				
	$C_7H_6(CH_3)_2N_3Cl.2AgI.$	I.	II.	III.	IV.	V.
C	16.19	18.00	17.82	17.61	....	....
H	1.8	1.8	1.77	1.75	....	....
N	6.29	....	....	....	4.99	....
Cl + I	43.37	....	....	....	....	39.54

This mixed formula is strongly supported by recent experiments which indicate the existence of narcotine compounds containing both chlorine and iodine.

The Conversion of Narcotine into Narceine.

As above mentioned, the process of converting narcotine-methyl iodide into the chloride, then into the hydroxide, and finally the latter, by intermutation, into narceine, involves a complex reaction whereby a large percentage of the chloride is converted into the azimido compound. By actual experiment, over 70 per cent of the narcotine-methyl iodide was lost. This fact was an incentive to search for a method by which a larger percentage of the narcotine could be converted into narceine. An examination showed that the loss occurred by treating with silver chloride. Direct substitution of iodine for chlorine was tried, and found to give very satisfactory results.

The following is the method adopted: Narcotine-methyl iodide was made by digesting narcotine with an excess of methyl iodide for ten hours. The excess of methyl iodide was then evaporated off on a water-bath and the residue dissolved in alcohol. The solution was treated with chlorine water. A light yellow substance was formed which was almost immediately dissolved in the alcohol. Upon addition of more chlorine water, more of the yellow substance was precipitated. With a slight excess of the reagent, the precipitate appeared to grow darker in color, and on standing a few minutes, the precipitate collected in flakes, and settled on the bottom, leaving the supernatant liquid with a brownish tinge. On warming for two or three hours, more of the precipitate dissolved, changing the liquid to a dark brown color. When the precipitate was first formed, no signs of crystallization were observed. However, on warming and allowing to stand for several hours, the precipitate appeared under the microscope as small prismatic needles. These crystals were filtered off, purified, and analyzed. The results of the analysis will be tabulated later on.

Narcotine-methyl chloride is very soluble in water, so that, if formed by the action of chlorine water on the iodide, it must necessarily be in the filtrate. The filtrate was, therefore, evaporated to dryness on a water-bath, a brownish, gum-like substance being left, which slowly changed into a crystalline mass. This substance was subsequently identified as pure narcotine-methyl chloride.

The method was then tried quantitatively with the following results :

I. 2.86 grams narcotine-methyl iodide gave 1.22 grams narcotine-methyl chloride.

II. 3.00 grams of narcotine-methyl iodide gave 1.39 grams narcotine-methyl chloride.

Later experiments have shown that a much larger percentage of the chloride can be obtained by using larger quantities of the iodide, thus reducing the relative loss. Fifty to sixty per cent can be obtained, or double the amount obtained by the old method.

In order to determine the purity of the chloride formed, a part was converted into the platinum double salt and examined. This salt is an amorphous powder, slightly soluble in water, and readily so in alcohol. When dried, it melted at 221° C. An analysis of the dried substance gave the following results :

I. 0.2090 gram double salt gave 0.0319 gram Pt.

II. 0.1946 gram double salt gave 0.0298 gram Pt.

	Calculated for $(C_{22}H_{23}NO_7.CH_3Cl)_2PtCl_4$.	Found. I.	Found. II.
Pt	15.39	15.27	15.31

The pure chloride thus obtained was then converted into narceine by the ordinary method of neutralizing with sodium hydroxide and passing a strong current of steam into the solution. On cooling, the whole solution became an almost solid mass of fine, felt-like crystals, which was readily recognized as narceine. The reaction was almost quantitative.

Narcotine-methyl Triiodide, $C_{22}H_{27}I_2NO_7.CH_3I$.—The formation of the brown substance already referred to, on the addition of chlorine water to the narcotine-methyl iodide, indicated that the change from the iodide to the chloride was not by direct substitution. In order to determine, as far as possible, the nature of the reaction, this by-product was examined. When first formed, it was of a dark brown color, and melted at 146° C., but, when recrystallized from alcohol and dried, it melted sharply at 149° C. The purified substance is almost insoluble in cold water, but soluble with difficulty in hot water. It dissolves readily in methyl and ethyl alcohols, from which it crystallizes in fine needles. It is likewise very soluble in chloroform, but, on evaporation, forms a brownish-red varnish. It is slightly soluble in ether and insoluble in carbon disulphide. The substance contains no water of crystallization. Analyses gave the following results :

I. 0.2082 gram of the substance gave 0.2583 gram CO_2, and 0.0633 gram H_2O.

II. 0.2473 gram substance gave 0.3081 gram CO_2, and 0.0723 gram H_2O.

III. 0.1995 gram substance gave 0.1754 gram AgI.

IV. 0.2036 gram substance gave 0.1803 gram AgI.

	Calculated for $C_{22}H_{21}I_2NO_7.CH_3I$.	Found. I.	II.	III.	IV.
C	34.25	33.83	33.98	....	....
H	2.98	3.38	3.25	....	....
I	47.12	....	....	47.50	47.84

From the large percentage of iodine found, it is evident that the iodine of the narcotine-methyl iodide has been concentrated in this by-product, three molecules, in the presence of chlorine, forming two of the chloride and one of the triiodide, according to the following equation :

$$3C_{22}H_{23}NO_7.CH_3I + 2Cl_2 = 2C_{22}H_{23}NO_7.CH_3Cl + C_{22}H_{21}I_2NO_7.CHI_3 + 2HCl.$$

The formation of hydrochloric acid in this reaction accounts for its presence in the liquid. According to the equation, three molecules of the narcotine-methyl iodide should give two molecules of narcotine-methyl chloride, or about 66 per cent, and one of the triiodide, or 33 per cent. The following determinations verify this equation :

I. 3 grams narcotine-methyl iodide gave 0.979 gram triiodide ; and 1.390 grams narcotine-methyl chloride.

II. 5 grams of narcotine-methyl iodide gave 1.64 grams of triiodide ; and 2.62 grams narcotine-methyl chloride.

As will be seen from the above equation, the highest per cent of the chloride obtainable, is 66, while by the silver chloride method, the formation of the azimido compound, makes only 25 per cent possible.

Methylnornarcotine-methyl Triiodide, $C_{20}H_{27}I_2NO_7.CH_3I$.—Repeated attempts to convert the triiodide into narcotine-methyl chloride were unsuccessful. It was noticed, however, while treating the triiodide with excess of chlorine water, that the melting-point of the brown precipitate was raised, and especially when heated on a water-bath with a large excess of chlorine. A maximum melting-point of 188° C. was finally reached.

According to Matthiessen and Foster,[1] concentrated hydrochloric acid converts narcotine into methylnornarcotine, liberating free methyl chloride. Inasmuch as a large amount of hydrochloric acid was liberated on treating the triiodide with strong chlorine water, it was suspected that this same reaction took place here. In order to examine this reaction more carefully, the following experiment was made : Ten grams of narcotine-methyl iodide were dissolved in a small quantity of alcohol and 200 cc. of strong chlorine water were added. Narcotine-methyl triiodide was formed. The whole mass was then placed on a water-bath and 600 cc. of strong chlorine water were added, a few cubic centimeters at a time. The heating was continued for twelve hours. At the end of that time the substance somewhat resembled the triiodide, except, perhaps, that it was a little darker. It was filtered off and recrystallized from alcohol. The crystals which first formed were of a reddish-brown color and belonged to the monoclinic system. These crystals, recrystallized from alcohol, melted sharply at 186° C. They are soluble in alcohol and chloroform, but insoluble in ether and petroleum ether.

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[1] J. Chem. Soc. (London), **21**, 357.

Analyses of the dried substance gave the following:

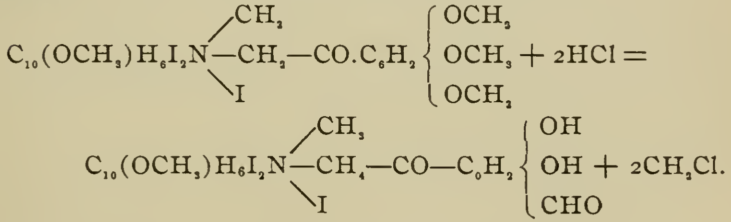
I. 0.2444 gram substance gave 0.2887 gram CO_2, and 0.0729 gram H_2O.

II. 0.2222 gram substance gave 0.2634 gram CO_2, and 0.0609 gram H_2O.

III. 0.2099 gram substance gave 0.1901 gram AgI.

	Calculated for $C_{30}H_{27}I_3NO_7.CH_3I$.	Found.		
		I.	II.	III.
C	32.34	32.22	32.32	....
H	2.57	3.31	3.30	....
I	48.90	....	....	48.93

It would therefore appear that chlorine water acts upon narcotine-methyl triiodide just as hydrochloric acid acts upon narcotine, removing two methoxyl groups from the opianic acid radical, but leaving the third, in the isoquinoline, unchanged. The reaction may be thus represented:



$$C_{10}(OCH_3)H_6I_2N\begin{array}{l}\diagup CH_3\\ -CH_2-CO.C_6H_2\\ \diagdown I\end{array}\left\{\begin{array}{l}OCH_3\\ OCH_3\\ OCH_3\end{array}\right. + 2HCl =$$

$$C_{10}(OCH_3)H_6I_2N\begin{array}{l}\diagup CH_3\\ -CH_4-CO-C_0H_2\\ \diagdown I\end{array}\left\{\begin{array}{l}OH\\ OH\\ CHO\end{array}\right. + 2CH_3Cl.$$

THE REACTION BETWEEN ALIPHATIC SULPHOCYANATES AND METALLIC DERIVATIVES OF ACETOACETIC ESTER AND ANALOGOUS SUBSTANCES.

BY ELMER P. KOHLER.

The aliphatic sulphocyanates react in a remarkably smooth and clean way with a number of substances which eliminate or replace the cyanogen group. The most important of these reactions are expressed by the following equations:

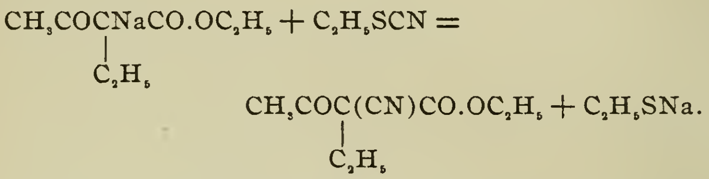
I. $2C_2H_5SCN + 2Na = (C_2H_5S)_2 + 2NaCN$;

II. $2C_2H_5SCN + K_2S = (C_2H_5S)_2 + KCN + KSCN$;

III. $2C_2H_5SCN + 2KOH = (C_2H_5S)_2 + KCN + KCNO + H_2O$;

IV. $C_2H_5SCN + 2NaSH = C_2H_5SNa + NaCN + H_2S$;
V. $C_2H_5SCN + NaSC_2H_5 = (C_2H_5S)_2 + NaCN$.

In all of these cases and in all other transformations of the sulphocyanates that have hitherto been studied, the cyanogen group is eliminated as the metallic cyanide or cyanate. In the reaction between the sulphocyanates and the metallic derivatives of the esters of ketonic acids the opposite takes place. In this case the primary reaction always results in the formation of a mercaptide and a cyanogen substitution-product of the ester:



$$CH_3CO\underset{\underset{C_2H_5}{|}}{C}NaCO.OC_2H_5 + C_2H_5SCN = CH_3CO\underset{\underset{C_2H_5}{|}}{C}(CN)CO.OC_2H_5 + C_2H_5SNa.$$

The final result depends, to some extent, upon the ester, the metal, and the sulphocyanate. If the resulting mercaptide is soluble in the liquid used as a medium, it immediately reacts with unchanged sulphocyanate:

$$C_2H_5SCN + NaSC_2H_5 = (C_2H_5S)_2 + NaCN.$$

The final result in the case of sodium ethylacetoacetic ester and ethyl sulphocyanate in absolute alcohol is, therefore, represented by the equation:

$$CH_3COCNa(C_2H_5)CO.OC_2H_5 + 2C_2H_5SCN = CH_3COC(CN)(C_2H_5)CO.OC_2H_5 + (C_2H_5S)_2 + NaCN.$$

In case the cyanogen derivative formed in the primary reaction contains hydrogen that is replaceable by metals, it passes into a metallic derivative by liberating a corresponding amount of the original ester; as the cyanogen compounds are invariably more strongly acid than the substances from which they are derived. With sodium acetoacetic ester, in absolute alcohol, for example, the reaction takes place according to the equation:

$$2CH_3COCHNaCO.OC_2H_5 + 2C_2H_5SCN = CH_3COCNa(CN)CO.OC_2H_5 + CH_3COCH_2CO.OC_2H_5 + (C_2H_5S)_2 + NaCN.$$

With sodium derivatives there are further complications due to the fact that sodium mercaptides, like sodium alcoholates, slowly saponify both the original esters and the cyanogen derivatives resulting from the reaction. In these cases the yield of cyanogen ester, under the most favorable circumstances, does not exceed 65 per cent of the amount calculated from the above reactions.

With the copper derivatives the reactions are perfectly clean, as the copper mercaptides are insoluble in organic liquids and inert. The reaction between copper acetoacetic ester and ethyl sulphocyanate, for example, takes place quantitatively, according to the equation :

$$\begin{aligned} &4(CH_3COCHCO.OC_2H_5)_2Cu + 4C_2H_5SCN = \\ &\qquad 2(CH_3COC(CN)CO.OC_2H_5)_2Cu + \\ &\qquad 4CH_3COCH_2CO.OC_2H_5 + (C_2H_5S)_2 + 2C_2H_5SCu. \end{aligned}$$

This equation may be separated into the following stages :

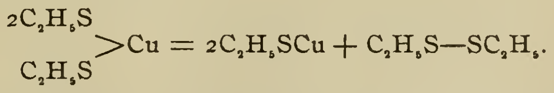
I. The primary reaction,

$$\begin{aligned} &(CH_3COCHCO.OC_2H_5)_2Cu + 2C_2H_5SCN = \\ &\qquad 2CH_3COCH(CN)CO.OC_2H_5 + (C_2H_5S)_2Cu. \end{aligned}$$

II. Because cyanacetoacetic ester is much more strongly acid than acetoacetic ester,

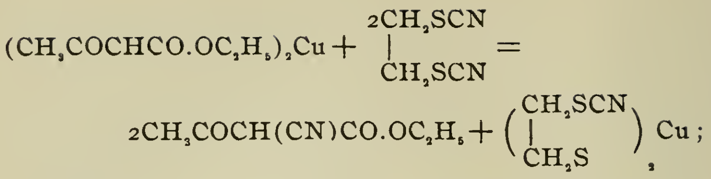
$$\begin{aligned} &(CH_3COCHCO.OC_2H_5)_2Cu + 2CH_3COCHCNCO.OC_2H_5 = \\ &\qquad (CH_3COC(CN)CO.OC_2H_5)_2Cu + 2CH_3COCH_2CO.OC_2H_5. \end{aligned}$$

III. Because cupric compounds with copper in direct union with sulphur are unstable,

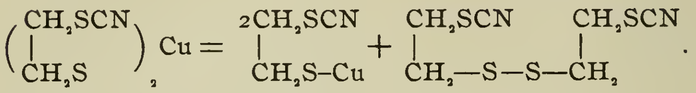


$$\begin{matrix} 2C_2H_5S \\ C_2H_5S \end{matrix}\!\!>Cu = 2C_2H_5SCu + C_2H_5S{-}SC_2H_5.$$

The reaction between copper derivatives and polysulphocyanates that have but one sulphocyanogen group with any one carbon atom, normally involves only one of the sulphocyanogen groups ; the remainder are protected by the insolubility of the resulting mercaptide. Ethylene sulphocyanate and copper acetoacetic ester, for example, in the cold, react according to the equations :

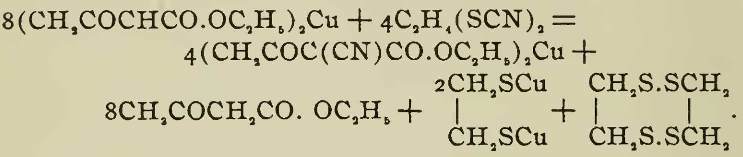


$$\text{I. } \mathrm{(CH_3COCHCO.OC_2H_5)_2Cu} + \begin{array}{l}\mathrm{2CH_2SCN}\\ |\\ \mathrm{CH_2SCN}\end{array} = \mathrm{2CH_3COCH(CN)CO.OC_2H_5} + \left(\begin{array}{l}\mathrm{CH_2SCN}\\ |\\ \mathrm{CH_2S}\end{array}\right)_2 \mathrm{Cu};$$



$$\text{II. } \left(\begin{array}{l}\mathrm{CH_2SCN}\\ |\\ \mathrm{CH_2S}\end{array}\right)_2 \mathrm{Cu} = \begin{array}{l}\mathrm{2CH_2SCN}\\ |\\ \mathrm{CH_2S\text{-}Cu}\end{array} + \begin{array}{lcl}\mathrm{CH_2SCN} & & \mathrm{CH_2SCN}\\ | & & |\\ \mathrm{CH_2} & \mathrm{—S—S—} & \mathrm{CH_2}\end{array}.$$

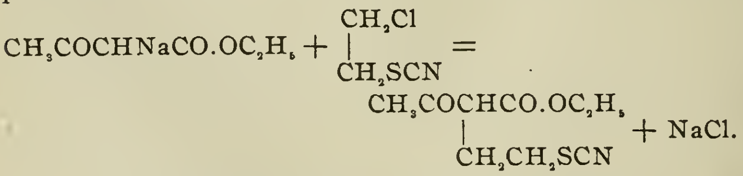
The sulphocyandisulphides thus formed are soluble in organic solvents, and at higher temperatures react like simpler polysulphocyanates. By adding the sulphocyanate, in very small quantities, to a saturated solution of the copper derivatives, all of the sulphocyanogen groups can be brought into reaction:



$$\mathrm{8(CH_3COCHCO.OC_2H_5)_2Cu} + \mathrm{4C_2H_4(SCN)_2} = \mathrm{4(CH_3COC(CN)CO.OC_2H_5)_2Cu} + \mathrm{8CH_3COCH_2CO.\ OC_2H_5} + \begin{array}{l}\mathrm{2CH_2SCu}\\ |\\ \mathrm{CH_2SCu}\end{array} + \begin{array}{ll}\mathrm{CH_2S.SCH_2} & \\ | & |\\ \mathrm{CH_2S.SCH_2} & \end{array}.$$

When polysulphocyanates have two sulphocyanogen groups in combination with the same carbon atom, both of them enter into reaction under all conditions.

A difference in the behavior with copper and sodium derivatives is observed in the case of halogen substitution-products of the sulphocyanates. With the former, chlorethylsulphocyanate reacts exactly like ethylsulphocyanate—the halogen does not enter into the reaction. With the latter, two reactions take place side by side—the normal reaction of the sulphocyanates and the general reaction of halogen substitution-products:



$$\mathrm{CH_3COCHNaCO.OC_2H_5} + \begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{CH_2SCN}\end{array} = \begin{array}{l}\mathrm{CH_3COCHCO.OC_2H_5}\\ \qquad\qquad |\\ \qquad\quad \mathrm{CH_2CH_2SCN}\end{array} + \mathrm{NaCl}.$$

I. Copperacetoacetic Ester and Ethylsulphocyanate.

Sixteen grams (1 molecule) of pure copper acetoacetic ester were dissolved in 500 cc. of boiling absolute alcohol; 4.5 grams (1 molecule) of ethyl sulphocyanate were added to this and the mixture heated in a water-bath. The solution almost immediately changed from the deep yellow-green color of copper acetoacetic ester to a light blue, and a curdy, cream-colored precipitate began to separate. After boiling for an hour the contents of the flask were almost solid. The liquid was drawn off as rapidly as possible and the boiling continued, but there was no further change.

The yellow precipitate was extracted with boiling absolute alcohol until the extract remained colorless. All the alcoholic solutions were then united, distilled to 500 cc. and allowed to cool. A dark-green copper compound crystallized out in small plates. The substance was washed with alcohol, dried at 100°, and analyzed without further purification:

I. 0.2354 gram substance gave 0.3940 gram CO_2, 0.0953 gram H_2O, and 0.0500 gram CuO.

II. 0.5145 gram substance gave 36.6 cc. N_2 at 16° and 753 mm.

III. 0.4555 gram substance gave 31.2 cc. N_2 at 15° and 753 mm.

	Calculated for $(C_7H_8O_3N_2)Cu$.	Found.		
		I.	II.	III.
C	45.3	45.6	..	..
H	4.3	4.3	..	..
N	8.3	...	8.2	8.0
Cu	17.0	17.0	..	..

The substance is pure coppercyanacetoacetic ester. It is difficultly soluble in boiling alcohol, benzene, acetone, ether, and carbon bisulphide. From a solution in any of these solvents it separates almost completely on cooling. It is insoluble in water and unlike copper acetoacetic ester, is not decomposed when boiled with water or aqueous alcohol. When heated in a capillary tube it remains unchanged until a temperature of about 250° is reached, when it melts with decomposition.

To liberate the ester the salt was warmed with dilute sulphuric acid and a little alcohol. The ester separated as a colorless liquid, which solidified on cooling. The melting-point of the solid was 26°, as found by Haller and Held.[1]

The light yellow precipitate was washed with ether and dried at 50°.

I. 0.2112 gram substance gave 0.1335 gram CuO.

II. 0.2214 gram substance gave 0.1395 gram CuO.

	Calculated for C_2H_5SCu.	Found. I.	II.
Cu	50.1	50.7	50.5

The substance is copper mercaptide. The high percentage of copper is due to a partial decomposition into mercaptan and copper hydroxide. It gave mercaptan when warmed with concentrated hydrochloric acid, and ethyl disulphide, boiling at 151°, when shaken with iodine and water.

The filtrate from the copper cyanacetoacetic ester was returned to the flask and all the alcohol removed by distillation. The residue was a thick liquid in which some of the copper compound was suspended. The liquid was drawn off and distilled. The temperature rapidly rose to 149°, where all of the liquid passed over. It was ethyl disulphide easily recognized by its boiling-point and the disulphide reaction.

All the alcoholic distillates were combined, fractioned with a Glinsky tube, and the last fraction and the residue treated with ammoniacal copper acetate. Copper acetoacetic ester separated on dilution with water, showing that acetoacetic ester is liberated during the reaction.

The four substances described are always formed when copper acetoacetic ester reacts with ethyl sulphocyanate, and they are the only products of the reaction. 64 grams of copper acetoacetic ester gave 33 grams of copper cyanacetoacetic ester and 11 grams of copper mercaptide. The equation given in the introductory part requires 34.8 grams of the former and 12 grams of the latter.

The course of the reaction cannot be changed by varying the relative amounts of the reacting substances or the conditions. The reaction takes place slowly in the cold, rapidly on heating. Any indifferent solvent may be used as a medium. Ordinary alcohol may be used if the temperature is kept below 70°. Above this point copper acetoacetic ester is rapidly decomposed by aqueous alcohol, apparently forming an oxy-compound analogous to the ethoxy compounds recently described by Wislicenus.[1]

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[1] Ann. Chim. Phys. (6), **17**, 204; Traube (Ber. d. chem. Ges., **31**, 3587) gives 36°, but this is probably a printer's error.

Methyl sulphocyanate, propyl sulphocyanate, isopropyl sulphocyanate, and benzyl sulphocyanate react like ethyl sulphocyanate. The reaction is, therefore, probably a general one for all aliphatic monosulphocyanates.

II. Copper Acetoacetic Ester and Ethylene Sulphocyanate.

Sixteen grams of copper acetoacetic ester (1 molecule) were gradually added to 15 grams of ethylene sulphocyanate (1 molecule), dissolved in cold absolute alcohol. At first only a grayish-white precipitate separated. After a few days copper cyanacetoacetic ester began to crystallize out along with the white substance. The separation continued slowly for three weeks, when the solution was almost colorless. The liquid was then filtered and the solid extracted with boiling absolute alcohol, which dissolved 8 grams of copper cyanacetic ester. The white residue, after extraction, was dried at 75° and analyzed.

I. 0.2421 gram substance gave 0.1770 gram CO_2, 0.0479 gram H_2O, and 0.1053 gram CuO.

II. 0.4220 gram substance gave 29.3 cc. N_2 at 17° and 755 mm.

III. 0.4515 gram substance gave 31.7 cc. N_2 at 17° and 756 mm.

	Calculated for $C_3H_4I_2NCu$.	Found. I.	II.	III.
C	19.74	19.9	..	..
H	2.02	2.2	..	..
N	7.7	...	8.0	8.1
Cu	35.02	34.8	..	..

The substance is a mixed mercaptide and sulphocyanate of ethane. It is insoluble in water and organic solvents. When boiled with alcoholic potassium sulphide it gives potassium sulphocyanate, proving the presence of the sulphocyanogen group. When boiled with concentrated hydrochloric acid it slowly dissolves as iminomethene-ethene disulphide hydrochloride:

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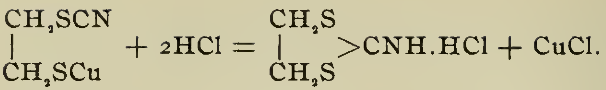
[1] Ber. d. chem. Ges., 31, 3151.



$$\begin{array}{l}CH_2SCN\\ |\\ CH_2SCu\end{array} + 2HCl = \begin{array}{l}CH_2S\\ |\\ CH_2S\end{array}\!\!>CNH.HCl + CuCl.$$

Fuming nitric acid oxidizes it to (1,2)-ethanedisulphonic acid.

The filtrate from the solid reaction-products was distilled from a water-bath to remove the alcohol, then with superheated steam to remove the acetoacetic ester. There remained a small quantity of unused sulphocyanate suspended in a thick colorless oil. The former was removed by repeated extraction with boiling water, the oil separated and dried over phosphorus pentoxide in a vacuum.

I. 0.3261 gram substance gave 0.3611 gram CO_2, and 0.1026 gram H_2O.

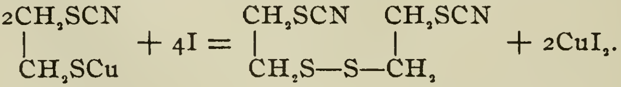
II. 0.3005 gram substance gave 0.3312 gram CO_2, and 0.0945 gram H_2O.

III. 0.4100 gram substance gave 42.7 cc. N_2 at 16° and 750 mm.

IV. 0.3112 gram substance gave 32.5 cc. N_2 at 16° and 750 mm.

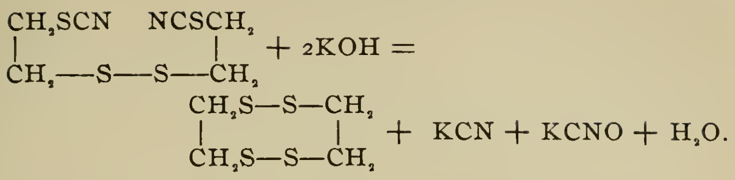
	Calculated for $C_6H_8O_4N_2$.	Found. I.	II.	III.	IV.
C	30.51	30.2	30.1	...	...
H	3.39	3.5	3.5	...	...
N	11.9	...	...	12	12.2

The substance is a colorless liquid which does not solidify at —20° and does not boil without decomposition. It is insoluble in water, moderately soluble in boiling alcohol and boiling benzene. It can readily be made in quantity by shaking the mercaptide, above described, with water and iodine :



$$2\begin{array}{l}CH_2SCN\\ |\\ CH_2SCu\end{array} + 4I = \begin{array}{lr}CH_2SCN & CH_2SCN\\ | & |\\ CH_2S{-}S{-} & {-}CH_2\end{array} + 2CuI_2.$$

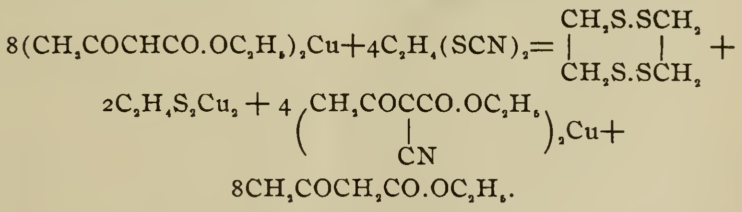
This proves that the substance is sulphocyanethyl disulphide. When warmed with strong potassium hydroxide it passes smoothly into ethylene tetrasulphide :



$$\begin{array}{l} CH_2SCN \qquad NCSCH_2 \\ | \qquad\qquad\qquad\quad | \\ CH_2—S—S—CH_2 \end{array} + 2KOH = \begin{array}{l} CH_2S—S—CH_2 \\ | \qquad\qquad\quad | \\ CH_2S—S—CH_2 \end{array} + KCN + KCNO + H_2O.$$

Sulphocyanmethyl disulphide does not react with copper acetoacetic ester in the cold. At the temperature of boiling alcohol the two react to form coppercyanacetoacetic ester and a mixture of complex sulphur compounds that are insoluble in all solvents. It was impossible to separate any pure substances from this mixture; but the amount of copper cyanacetoacetic ester obtained shows that only one of the sulphocyanogen groups is attacked. The reaction is, therefore, similar to that with ethylene sulphocyanate. This explains what happens when the alcoholic solution of 1 molecule of ethylene sulphocyanate and 1 molecule of copper acetoacetic ester is boiled—the disulphide reacts as fast as formed and the final result is copper cyanacetoacetic ester, which can be extracted with alcohol, the copper salt of sulphocyanethylmercaptan, which can be removed with boiling hydrochloric acid, and the complex mixture just described.

If 1 molecule of ethylene is very gradually added to 2 molecules of copper acetoacetic ester in boiling absolute alcohol both of the sulphocyanogen groups enter into the reaction:



$$8(CH_3COCHCO.OC_2H_5)_2Cu + 4C_2H_4(SCN)_2 = \begin{array}{l} CH_2S.SCH_2 \\ | \qquad\quad | \\ CH_2S.SCH_2 \end{array} + 2C_2H_4S_2Cu_2 + 4\left(\begin{array}{c} CH_3COCCO.OC_2H_5 \\ | \\ CN \end{array}\right)_2Cu + 8CH_3COCH_2CO.OC_2H_5.$$

Sixteen grams of copper acetoacetic ester were dissolved in 1000 cc. boiling absolute alcohol and 7 grams of ethylene sulphocyanate, likewise dissolved in 1000 cc. absolute alcohol, added drop by drop. After boiling for ten hours the liquid was filtered. The alcoholic solution contained only copper cyanacetoacetic ester and acetoacetic ester. The light yellow solid, insoluble in alcohol, was digested with concentrated hydrochloric acid for five hours and the solution distilled with steam. Pure ethylene mercaptan was obtained. The residue insoluble in hydrochloric acid was ethylene tetrasulphide, melting at 151°, and in every respect identical with a specimen prepared by warming ethylene sulphocyanate with a strong solution of potassium hydroxide.

(1,2)-Disulphocyanpropane and (1,3)-disulphocyanpropane react like (1,2)-sulphocyanethane.

III. Copper Acetoacetic Ester and Methylene Sulphocyanate.

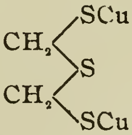
Six and a half grams of methylene sulphocyanate were added to 16 grams of copper acetoacetic ester dissolved in absolute alcohol. No reaction took place in the cold. On warming, a dark brown precipitate formed. After boiling for five hours the liquid was filtered, the precipitate extracted with boiling alcohol, and dried on a water-bath. The alcoholic solution contained 8.2 grams of copper acetoacetic ester, showing that both of the sulphocyanogen groups had entered into the reaction. An analysis of the precipitate gave the following results:

I. 0.5221 gram substance gave 0.1158 gram CO_2, 0.0474 gram H_2O, and 0.3994 gram CuO.

II. 0.4811 gram substance gave 0.1058 gram CO_2, 0.0304 gram H_2O, and 0.3667 gram CuO.

	Calculated for $CH_2S_2Cu_2$.	Found. I.	II.
C	5.84	6.1	6.0
H	0.97	1.01	0.7
Cu	61.5	61.2	61.0

The substance has the composition of copper methylene-mercaptide and seems to be perfectly homogeneous. It may, however, be a mixture of cuprous sulphide and the mercaptide



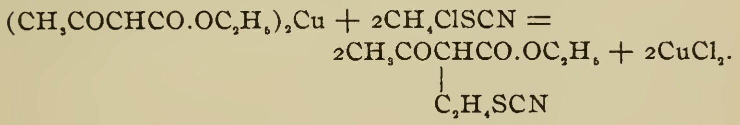
This would account for the dark color and the behavior with hydrochloric acid. When the substance is allowed to stand with concentrated hydrochloric acid, hydrogen sulphide is given off, cuprous chloride goes into solution, and the mercaptide referred to is left as a light yellow, impalpable powder:

0.4044 gram substance gave 0.1378 gram CO_2, 0.0618 gram H_2O, and 0.2542 gram CuO.

	Calculated for $C_2H_4S_3Cu_2$.	Found.
C	9.55	9.3
H	1.59	1.7
Cu	50.7	50.3

IV. Copper Acetoacetic Ester and Chlorethyl Sulphocyanate.

Varying quantities of chlorethyl sulphocyanate were heated with copper acetoacetic ester, to determine whether it is possible to get a reaction according to the equation:

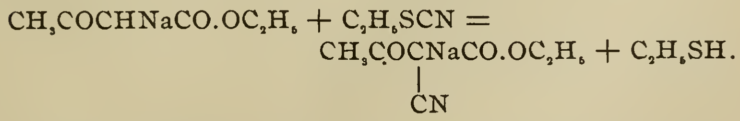


$$(CH_3COCHCO.OC_2H_5)_2Cu + 2CH_4ClSCN = 2\underset{\displaystyle C_2H_4SCN}{CH_3COCHCO.OC_2H_5} + 2CuCl_2.$$

In all cases the reaction was the same as with ethyl sulphocyanate. No cuprous chloride could be detected and the amount of copper cyanacetoacetic ester obtained agreed closely with the amount calculated.

V. Sodium Acetoacetic Ester and Ethyl Sulphocyanate.

The reactions with sodium acetoacetic ester are not nearly as clean as those with copper acetoacetic ester as the sodium mercaptide formed, like sodium ethylate, decomposes both the unchanged acetoacetic ester and the cyanacetoacetic ester, which is a product of the reaction. If, for example, acetoacetic ester, sodium alcoholate, and a sulphocyanate are brought together in molecular quantities in absolute alcohol, the yield of cyanacetoacetic ester never exceeds 15 per cent of the amount calculated from the equation:



$$CH_3COCHNaCO.OC_2H_5 + C_2H_5SCN = CH_3CO\underset{\displaystyle CN}{C}NaCO.OC_2H_5 + C_2H_5SH.$$

The by-products are, in this case, sodium acetate and sodium carbonate from acetoacetic ester, and ethyl disulphide and sodium cyanide formed by the action of sodium mercaptide on the sulphocyanate,

$$C_2H_5SCN + NaSC_2H_5 = (C_2H_5S)_2 + NaCN.$$

A somewhat better yield was obtained by mixing acetoacetic ester with benzene, and alternately adding small quantities of dry sodium alcoholate and ethyl sulphocyanate until the three substances were present in molecular quantities. The mixture was allowed to stand for several days, then poured into water and carefully acidified with dilute acetic acid. The benzene solution contained only ethylmercaptan and a small quantity of ethyl disulphide. The aqueous solution, on evaporation, gave a 32 per cent yield of sodium cyanacetoacetic ester and a small quantity of sodium cyanide.

The best results were obtained by bringing together pure, dry sodium acetoacetic ester and an excess of the sulphocyanate in absolute ether, and allowing the mixture to stand in the cold. 45 grams of ethyl sulphocyanate were added to 75 grams of sodium acetoacetic ester suspended in 750 cc. ether, and the mixture allowed to stand for two weeks. A part of the ether was removed by distillation, the residue poured into water and acidified with acetic acid. After separating the aqueous solution it was acidified with sulphuric acid and repeatedly extracted with small quantities of ether. This ethereal solution, when separated by fractional distillation under diminished pressure, gave 42 grams of cyanacetoacetic ester—a yield of about 60 per cent.

VI. Sodium Ethyl Acetoacetic Ester and Ethyl Sulphocyanate.

In all the experiments hitherto described, one of the products was a metallic derivative of acetoacetic ester. To determine whether the reaction is possible when it involves the formation of an ester which contains no hydrogen replaceable by metals, molecular quantities of ethyl acetoacetic ester, dry sodium alcoholate, and ethyl sulphocyanate were brought together in absolute ether. After standing for two weeks, the resulting mixture was separated and the products purified as in the preceding experiment. A 22 per cent yield of cyanethylacetoacetic ester was obtained. The ester boiled at 130° at a pressure of about 35 mm; and the analyses show that it was pure.

I. 0.2185 gram substance gave 0.4702 gram CO_2, and 0.1390 gram H_2O.

II. 0.2213 gram substance gave 0.4771 gram CO_2, and 0.1413 gram H_2O.

III. 0.4216 gram substance gave 28.5 cc. N_2 at 17° and 755 mm.

	Calculated for $C_9H_{13}O_3N$.	Found. I.	II.	III.
C	59.01	58.7	58.8	...
H	7.1	6.9	7.1	...
N	7.65	...	...	7.8

VII. Sodium Acetoacetic Ester and Chlorethyl Sulphocyanate.

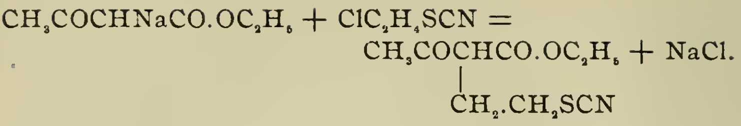
A solution of sodium acetoacetic ester was prepared by dissolving 11.5 grams of sodium in 200 cc. of absolute alcohol and adding 65 grams of acetoacetic ester. 65 grams of chlorethyl sulphocyanate were added to this solution. The resulting liquid was boiled, with inverted condenser, until the reaction was neutral to litmus. The alcohol was removed and the residue poured into water when a heavy brown oil separated. This was washed with a dilute solution of sodium hydroxide until the washings were colorless. The oil was separated and cooled in ice-water, when most of it solidified. The solid was dried on plates and purified by recrystallization from petroleum ether. It was thus obtained in colorless, transparent plates or needles melting sharply at 83°.

I. 0.3115 gram substance gave 0.5716 gram CO_2, and 0.1678 gram H_2O.

II. 0.4623 gram substance gave 30.2 cc. N_2 at 28.5° and 744 mm.

	Calculated for $C_9H_{13}O_3SN$.	Found. I.	II.
C	50.2	50.1	...
H	6.05	6.0	...
N	6.51	...	6.9

The substance is sulphocyanethylacetoacetic ester, formed according to the equation:



$$CH_3COCHNaCO.OC_2H_5 + ClC_2H_4SCN = \underset{CH_2.CH_2SCN}{CH_3COCHCO.OC_2H_5} + NaCl.$$

The substance is insoluble in water, moderately soluble in petroleum ether, very soluble in alcohol, ether, and benzene. It reacts with copper acetoacetic ester to form copper cyanacetoacetic ester and a mercaptide, proving the presence of a sulphocyanogen group. 30 grams of the substance were obtained from 65 grams of acetoacetic ester.

The aqueous solution, separated from the oil, was decolorized with bone-black and evaporated to crystallization. It gave 38 grams of sodium cyanacetoacetic ester.

BRYN MAWR COLLEGE.
CHEMICAL LABORATORY.

A METHOD FOR CARRYING OUT CHEMICAL REACTIONS UNDER HIGH PRESSURES.

BY B. H. HITE.

The great majority of chemical reactions are carried out under ordinary, or atmospheric, pressures, which happen to be really very low pressures. Even in the comparatively few cases in which somewhat higher pressures are used, as those accomplished in an autoclave or Carius tube, the effect of the pressure cannot be determined on account of the elevation of temperature necessary to obtain the pressure. There is no convenient practical method, certainly none in general use, that is independent of the temperature and applicable to a very wide range of pressures. The lack of such a method or apparatus is the more noticeable in view of the long list of devices available for studying the effect of temperature. That most reactions are far more susceptible to slight changes of temperature than to what might perhaps be regarded as comparable changes in pressure is doubtless true, and it may be that the relative importance of these two agents is indicated fairly enough by the usual laboratory equipment, and yet before taking this for granted it would seem that, inasmuch as available temperatures have been extended to the fusing-point of carbon, there ought to be one method, at least, in which available pressures would be limited only by the crushing strength of steel.

Such a method should be applicable to reagents in solution, in quantities suitable for experimental purposes, and, if possible, in glass or platinum vessels. There must be no leaking under the pressure applied, which must be absolutely independent of the temperature used. A description of such a method follows :

A platinum tube T, Fig. 1, 4 inches long by $\frac{3}{4}$ inch in diameter, and similar generally to the ordinary collapsible lead (or tin) paint tubes is filled with the solution of the reagents, closed with a stopper or screw cap, and placed in a lead tube about $1\frac{1}{4}$ inches in diameter by 5 or 6 inches long. The lead tube (see also Fig. 2) is then filled with water, closed with a lid L, and placed in a steel cylinder C, about 7 inches long by 6 inches in diameter, with a hole through it about $1\frac{1}{4}$ inches in

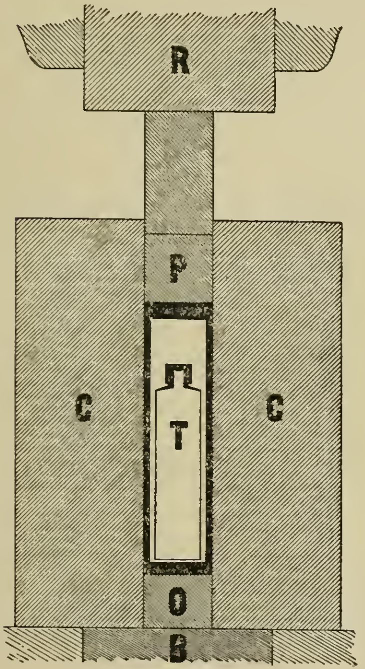


Fig. 1.

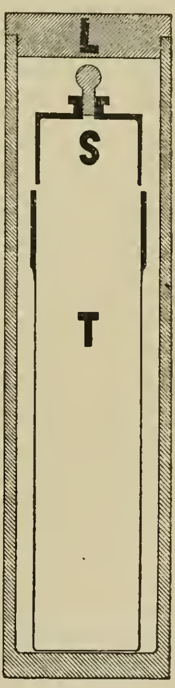


Fig. 2.

diameter. The lead tube rests on a steel plug O, which closes the lower end of the cylinder and rests on the bed-plate B, of a powerful hydraulic press, while the pressure exerted by the ram R of the press is communicated by means of a steel piston P to the lead tube and its contents.

The platinum tube simply serves to separate the reagents within from the water surrounding it. It may be made very similar to the collapsible tubes mentioned : indeed these tubes may be very conveniently substituted whenever the reagents to be used will not attack them. Several thousand of these tin tubes were used in studying the effect of pressure on solutions containing bacteria, and found to be entirely satisfactory. The platinum tubes should be made of very thin foil, so that on relieving the pressure the liquid within the tubes, expanding to its original volume, may not injure the screw caps or displace the stopper used in closing the tubes. The wide-mouth tube T, shown in Fig. 2, is a very convenient form, as it is easily filled and emptied, and the dents which have a tendency to accumulate may be easily removed. The walls of this tube are reinforced for about an inch from the mouth to make them firm enough to hold the stopper S, which is provided with a small opening through which may escape any excess of solution, or any air bubbles that might otherwise be enclosed, thus permitting the stopper to be forced securely into the mouth of the tube, when the small opening is closed, as shown, with a small platinum plug.

The lead tube, which is the packing of this device, is securely sealed by the pressure so that *the liquid is completely encased in one continuous piece of metal.* It is this continuous metal packing that is responsible for the high pressures obtainable by this method. On removing the pressure, the water, in expanding to its original volume, will sometimes loosen the lid of the lead tubes, and if a high pressure has been used the lead tube, in stretching to its original capacity, will sometimes be pulled completely in two ; but as nothing but water can escape in either case these are not serious matters. There is absolutely no trace of leak while the liquid is under pressure.

The cylinder C should be made of the very finest tool steel.

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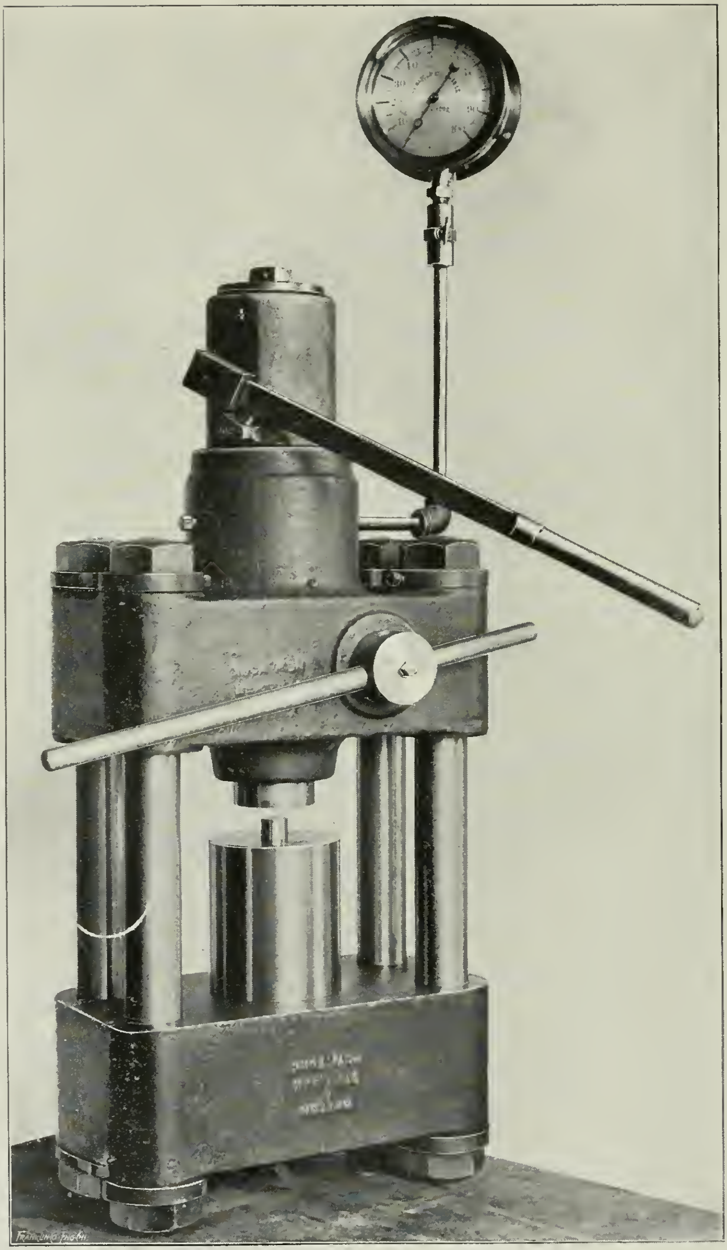

Fig. 3.

The hole through it must be true and smooth, and must fit accurately the plugs or pistons, O and P, which must also be made of the very finest tool steel and tempered hard. Just how hard the cylinder should be tempered seems to depend upon the kind of steel used. The cylinders must be hard enough to keep their shape, and yet if tempered too hard they are likely to contain a number of very fine cracks imperceptible at first, but which will open a little wider with each application of the pressure until the cylinder gives way. The best results were obtained with cylinders made of a special steel which, without much tempering, is hard enough to keep its shape. Most of the cylinders were "built up" of a number of concentric cylinders shrunk together, the object being to make the outer part of the cylinder carry more of the strain than it would if made of one piece.

With cylinders of the dimensions named, reactions have been carried out under a pressure of 200,000 pounds to the square inch, but having forced a cylinder of this size (1¼ inch bore) to such a pressure once, it is by no means safe to conclude that it will stand the same pressure again, for it may burst under a much lower pressure. Even the hard tool steel plugs and pistons have been crushed by such pressures, so it would seem that the limit had been reached, at least for cylinders of this size. If higher pressures are desired, cylinders of smaller bore must be used. A three-fourths inch bore will be found very convenient for pressures of about 200,000 pounds to the square inch. A one-half inch bore is the smallest that has been used by the writer. With cylinders of this size pressures of over 400,000 pounds to the square inch have been obtained, but in such tests the tool steel pistons were completely crushed.

The ram R of the press must be made of hard steel and a block B of the same material should be embedded in the lower platten of the press. The "four-rod, punch-type" hydraulic press, shown in Fig. 3, is a very convenient machine with which to apply and measure the pressures. It weighs about 1,000 pounds and has a capacity of considerably more than 100 tons. The pressure is applied and relieved by means of the upper lever shown in the cut. The ram is quickly raised or lowered with the lower lever.

It will be observed that there is ample room in this press for inclosing the cylinder within a jacket or bath by means of which the effect of a wide range of temperature may be studied in connection with the pressure, and, that the application of each is entirely independent of the other.

A testing machine may be used to furnish and measure the pressure. In order that the method might be applicable to long-continued pressures without being limited to one determination at a time, and without leaving the press so long under a strain, the cylinder shown in Fig. 4 was devised. It is somewhat longer than the one just described, and the bore is abruptly decreased at a point a short distance above the bottom forming a shoulder upon which rests the lower plug O. The piston P is also provided with a shoulder which enables the pressure (after being applied as before) to be carried by the heavy screw S. In order to open this cylinder it will be necessary to put it back into the press and apply enough pressure to the piston to relieve the screw, which is then removed, and the piston, the lead tube, and the plug O are pushed out with a steel rod applied through the hole in the bottom of the cylinder. This cylinder has another advantage, especially when a testing machine is used, in that it may be inverted or shaken so as to mix the reagents while they are under pressure. This is desirable in working with reactions which readily take place under ordinary pressures, but which are suspected of taking a different course under higher pressures. In such cases the reaction should not begin until the pressure

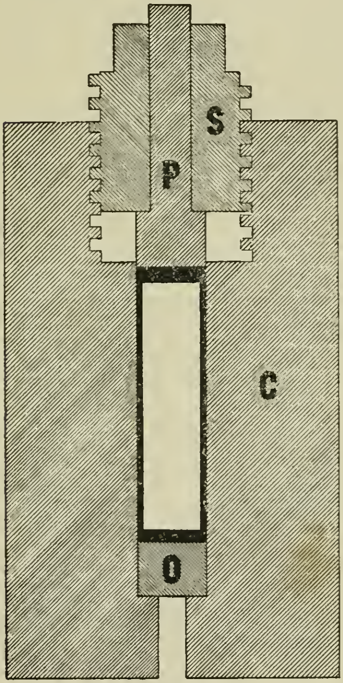

Fig. 4.

is applied. Several methods for accomplishing this will suggest themselves; among them the following: the reagents are dissolved in two separate portions of the solvent, the solution of higher specific gravity poured into the platinum tube first, then the other portion is introduced carefully so as not to mix the two. After the pressure is applied and secured by the screw, the cylinder is inverted. This may, however, be accomplished just as easily in the simpler cylinder first described and with the advantage of an unbroken record of the pressure, if the press is supported so that it may be tilted. Of course, in working with reactions which do not take place until higher pressures or temperatures than ordinary have been applied, no such precautions will be necessary.

A cylinder that may be very conveniently used in many lines of work is shown in Fig. 5. It is made much lighter than those described and is not intended for pressures of more than about 25 tons per square inch. It will be observed that the pressure may be secured by the screw and so continued indefinitely after removing from the press; also that the lower end of the cylinder is permanently closed. In this cylinder a solid block of lead (indicated in the section by the solid rectangle) serves as the packing. It rests on an offset or shoulder, the space below it being filled with water, and the platinum tube containing the reagents. The piston forces the lead down into the cylinder, compressing the water and preventing its escape. In order to open the cylinder the piston and packing must be pulled out. The piston can be easily removed if fastened in a vise. The packing may be removed by a screw, the head of which is held in a vise. These would not be the comparatively easy operations they are, but for the fact that the water in expanding gives the packing and piston a decided start.

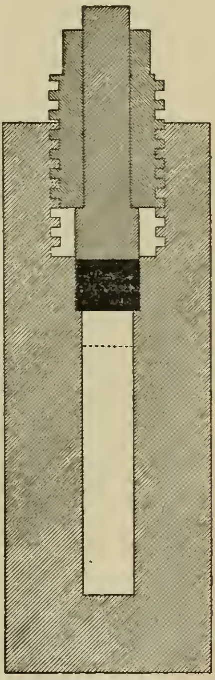

Fig. 5.

One person can open and charge 10 or 12 cylinders in an hour.

A certain amount of pressure is always required to force the lead packing past the shoulder, and in order to measure accurately the net pressure on the water, a hole is drilled through the side of the cylinder, and a piece of tubing leading to a gauge is attached directly. A gauge attached in this way to a cylinder containing a liquid under pressure is extremely sensitive to changes in temperature, and if a constant pressure is to be maintained *after the cylinders are taken from the press*, the temperature must not change. These low pressure cylinders would certainly be convenient substitutes in many cases for autoclaves or sealed tubes. Of course other metals (or alloys) than lead may be used as packing and other liquids than water may be used to communicate the pressure to the platinum tube and its contents.

The above method was worked out in connection with a study of the effect of pressure on bacteria in milk, meats, fruit juices, and other perishable food-stuffs. At odd moments, while this work was going on, the effect of pressure on a number of chemical reactions received attention, and these will be reported in the near future.

West Virginia Agricultural
Experiment Station,
Morgantown, W. Va.

NOTE.

A New Test for Cocaine.

There are two well-known tests for determining the freedom of commercial cocaine salts from other coca alkaloids. These are the permanganate test for detecting cinnamyl-cocaine, and the ammonia test, popularly known as McLagan's test, for detecting the presence of the coca alkaloids which are resistant to permanganate.

While it is generally admitted that the permanganate test is sufficient to detect the presence of cinnamyl compounds, chemists have expressed some doubt regarding the value of McLagan's test. The writer has for some time been conducting experiments with the object of finding a substitute for McLagan's test which would allow of the rapid and accurate determination of the presence in cocaine salts of the coca alkaloids not indicated by the permanganate test.

As the result of numerous determinations, I have devised a test based on the fact that the chromates of these alkaloids are much less soluble than cocaine chromate, both in water and in water acidulated with hydrochloric acid. The relative solubility of the chromates in acidulated water is about 1 to 500 in the case of cocaine chromate, and 1 to 5000 in the case of residual alkaloidal chromates.

I therefore offer the following as a simple and satisfactory method of determining the purity of cocaine salts: 0.05 gram cocaine hydrochloride is dissolved in 20 cc. of distilled water, mixed with 5 cc. of a 3 per cent solution of chromic acid, and to the mixture 5 cc. of a 10 per cent solution of hydrochloric acid are added. It is advisable to keep the temperature of the solution at 15° C. If the cocaine hydrochloride is pure a clear solution will result. If other than traces of foreign coca bases are present the solution becomes cloudy at once, or in a few minutes, according to the amount of impurity present.

It is advisable to make the test side by side with a specimen of known purity for comparison.

GEORGE L. SCHAEFER.

N. Y. QUININE AND CHEMICAL WORKS,
March 27, 1899.

OBITUARY NOTICE.

CHARLES FRIEDEL. (1832–1899.)

In the death of Charles Friedel, at the age of sixty-seven, which occurred April 20th, France lost one of her best known chemists. He manifested a talent for science at an early age, an inheritance perhaps from his grandfather, Dr. Duvernoy, who was a man of scientific attainments, and at the time of his death was recognized as a man well worthy of the high honors which had been bestowed upon him. After taking the degree of B.S., with honors he came under the influence and inspiration of Wurtz. He was made Doctor of Science in 1869, instructor at École Normale Supérieure in 1871, Professor of Mineralogy at the Sorbonne in 1876, Member of the Institute in 1878, and Professor of Chemistry, to succeed Wurtz, in 1884. He was the holder of several honorary degrees from the English Universities and in 1880 he was awarded the Davy Medal by the Royal Society. In him was combined both the skill of the investigator and the inspiring enthusiasm and clear logical presentation of the teacher.

His contributions to science, which have appeared in about 100 papers, relate mainly to organic chemistry. After his first paper, which appeared in 1876 on acetone, he extended the work to other compounds containing three carbon atoms, and also did much to advance the ideas of Kekulé on the structure of carbon compounds. Evidence confirming the views of Kekulé as to the quadrivalence of carbon resulted from his work on silicon and titanium, which he showed were similar in their chemical behavior to carbon and quadrivalents. His name is perhaps best known from his connection with the so-called Friedel-Crafts reaction. These chemists showed that a hydrocarbon residue could be readily introduced into many substances by treating a hydrocarbon with a chlorine derivative in the presence of aluminium chloride. Friedel was also greatly interested in the practical side of chemistry, was the founder of the French Association for the Advancement of Science, and acted as President of the Congress on Chemical Nomenclature which met at Geneva in 1892.

J. E. G.

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VOL. XXII. AUGUST, 1899. NO. 2.

AMERICAN
CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

CXV.—ON NITROMALONIC ALDEHYDE.

BY HENRY B. HILL AND JOSEPH TORREY, JR.

INTRODUCTION.

BY HENRY B. HILL.

In 1882 Hill and Sanger[1] published a preliminary notice describing briefly certain bodies which they had obtained by the action of alkaline nitrites upon mucobromic acid and its esters. When an alcoholic solution of mucobromic acid was added to a solution of potassic nitrite in diluted alcohol, reaction soon set in, the solution became deep-red, carbonic dioxide was evolved, and, as the solution cooled, an orange-red potassium salt separated which had the formula $K_2C_3HN_3O_7$. While this salt was quite stable in alkaline solution, and could readily be recrystallized from warm water on the addition of a small quantity of potassic hydrate, it was rapidly decomposed when heated in neutral aqueous solution; a complicated reaction set in, in which carbonic dioxide was evolved, hydrocyanic acid formed, and at the same time a colorless potassium salt, which crystallized in well-formed prisms as the solution cooled; this colorless salt was shown to have the formula $KC_3H_2NO_4.H_2O$. With sodic nitrite the reaction proved to be similar, except that in this case no deeply colored intermediate compound could be isolated; the main product formed was a colorless sodium salt which had the composition $NaC_3H_2NO_4.H_2O$, and corresponded to the colorless potassium salt already obtained. With ethyl mucobromate a reaction of entirely different character took place ; in this case no carbonic dioxide was formed, while the bromine was completely removed, and if potassic nitrite was used, a sparingly soluble, highly crystalline, and stable salt was formed which had the formula $KC_6H_6NO_6$. The mode of formation and the behavior of these three sets of salts warranted the conclusion that they all contained the nitro group, but no facts were discovered which threw further light upon their constitution. From the sodium salt, $NaC_3H_2NO_4.H_2O$, a number of other salts were made by double decomposition, and while these salts were not especially stable, no suspicion was entertained at the time that they were not salts of a nitro acid of ordinary type. The study of these bodies was unavoidably interrupted soon after the publication of this preliminary note, and on account of the press of other work the subject received no further attention for many years. Although the negative results which Hill and Sanger had obtained made the outlook appear rather unpromising, Dr. Torrey was interested several years ago to continue the investigation with me, and a brief note containing some of our results has already appeared.[1]

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[1] Ber. d. chem. Ges., 15, 1906.

We chose as our starting point the colorless salt which is apparently the final product of the action of alkaline nitrites upon mucobromic acid in alcoholic solution. A study of this, the most stable, and at the same time the most simple body formed in the reaction, could hardly fail to give a clue to the structure of the more complicated products. Since the sodium salt is more easily and economically prepared than the potassium salt, we have used it in all our work. We found at the outset that we could get no well-defined derivatives either by reduction or oxidation, and that the free acid could not be isolated from aqueous solution by the ordinary methods. On the addition of aniline hydrochlorate to an aqueous solution of the sodium salt, a bright yellow, highly crystalline compound was soon formed, which could readily be recrystallized from alcohol. This body proved to have the formula $C_9H_8N_2O_3$, so that an atom of oxygen in the body $C_3H_3NO_4$, from which the sodium salt is derived, had been removed and replaced by the phenylimido group. While this body was not further attacked by aniline hydrochlorate, aniline readily removed a second atom of oxygen and formed the body $C_{15}H_{12}N_3O_2$. The latter compound could be made more easily by the direct action of aniline dissolved in diluted alcohol upon the sodium salt. The formation of these two aniline derivatives by the successive replacement of oxygen by the group C_6H_5N rendered it extremely probable that the sodium salt itself contained two aldehyde groups :

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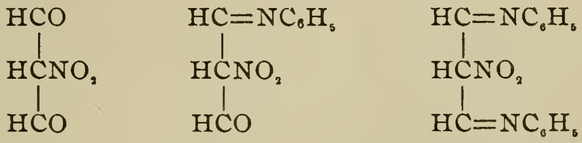
[1] Ber. d. chem. Ges., 28, 2597.



$$\begin{array}{ccc} \mathrm{HCO} & \mathrm{HC{=}NC_6H_5} & \mathrm{HC{=}NC_6H_5} \\ | & | & | \\ \mathrm{HCNO_2} & \mathrm{HCNO_2} & \mathrm{HCNO_2} \\ | & | & | \\ \mathrm{HCO} & \mathrm{HCO} & \mathrm{HC{=}NC_6H_5} \end{array}$$

With *p*-toluidine the analogous derivatives were easily obtained, and methylamine, ethylamine, or isoamylamine also formed similar compounds. As might have been expected, we obtained with phenylhydrazine bodies which were precisely analogous to the aniline derivatives ; their isolation required more care, however, since they were easily decomposed with the formation of a substituted pyrazol, while we had been unable to convert the aniline derivatives into a substituted quinoline, the formation of which from β-diketones under similar conditions had previously been observed.[1] When phenylhydrazine hydrochlorate was added to an aqueous solution of the sodium salt a yellow hydrazone soon separated in clustered prisms, while phenylhydrazine itself gave under the same conditions finely felted needles of the sodium salt of the dihydrazone. This sodium salt was decomposed even by carbonic dioxide with the liberation of a brilliant red dihydrazone. When either of these two phenylhydrazones is dissolved in boiling alcohol, a substance crystallizes as the solution cools which has the composition of a phenylnitropyrazol. This well-crystallized and remarkably stable body gave in unmistakable fashion the pyrazol reaction described by Knorr,[2] when it was reduced in alcoholic solution by sodium, and the product oxidized with potassic dichromate after acidification with sulphuric acid. This behavior of the sodium salt toward phenylhydrazine, since it is identical with that shown by β-diketones and keto-aldehydes of known structure, was sufficient to establish it as a derivative of nitromalonic aldehyde :

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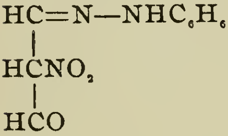
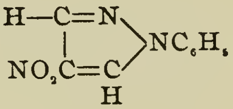
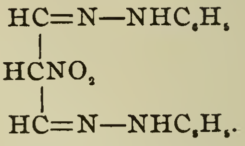
[1] Ber. d. chem. Ges., **20**, 1767; **28**, 1038; Compt. rend., **106**, 142.

[2] Ann. Chem. (Liebig), **238**, 200.



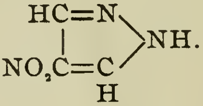
$$\begin{array}{l} HC{=}N{-}NHC_6H_5 \\ \vert \\ HCNO_2 \\ \vert \\ HCO \end{array}$$





$$\begin{array}{l} HC{=}N{-}NHC_6H_5 \\ \vert \\ HCNO_2 \\ \vert \\ HC{=}N{-}NHC_6H_5. \end{array}$$

Since the phenylnitropyrazol thus prepared had not previously been described, and its structure was therefore to a certain extent a matter of conjecture, it seemed of interest to prepare by the action of hydrazine the corresponding nitropyrazol. This body was first made by Buchner and Fritsch,[1] and its constitution was later established by Hantzsch,[2] who showed that it contained its nitro group upon the central carbon atom. We have made no extended study of the products formed by the action of hydrazine upon the sodium nitromalonic aldehyde, but we have shown that a nitropyrazol is readily formed through a secondary reaction, and that this product is evidently identical with the 4-nitropyrazol of Buchner.



Hydroxylamine reacts promptly in alkaline and neutral solution with sodium nitromalonic aldehyde, but we have had great difficulty in obtaining satisfactory results in the study of the products formed. If hydroxylamine hydrochlorate is added to a concentrated aqueous solution of the salt, a colorless, neutral body is thrown down, which from its composition and its neutral character must be considered as the β-nitroisoxazol, corresponding to the bodies described by Claisen[3] and his pupils as formed under similar conditions from β-diketones and keto-aldehydes. With free hydroxylamine in concentrated aqueous solution the sodium salt of a dioxime is formed, but the dioxime itself seems incapable of separate existence. On careful acidification of this sodium salt, a complex reaction ensues which is at present under investigation. A more complete description of the derivatives of both these oximes must be reserved for a subsequent paper.

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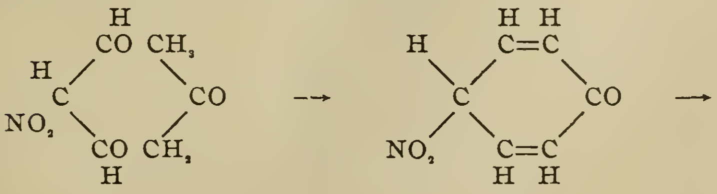
[1] Ann. Chem. (Liebig), **273**, 265.

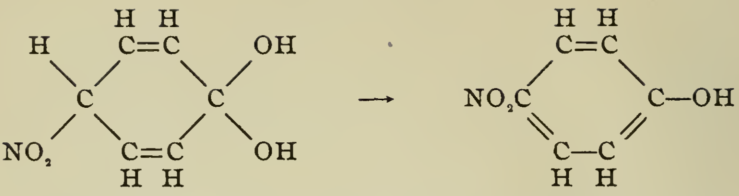
[2] *Ibid.*, **279**, 228.

[3] Ber. d. chem. Ges., **21**, 1149 ; **21**, 2178 ; **24**, 130 ; **24**, 3900.

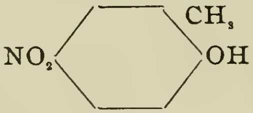
The whole behavior of the sodium salt in question is, therefore, in accordance with the supposition that it is a derivative of nitromalonic aldehyde. The question of the position of the sodium atom did not at first interest us directly, since this is evidently the same as that in the analogous salts of the nitroparaffins. Later we attempted to obtain evidence upon this point, but our experiments had been brought to no satisfactory conclusion when other investigations upon the same subject appeared, and we have not carried them farther.

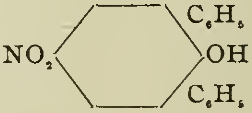
In order to show still more conclusively that our substance was a double aldehyde, it seemed advisable to involve both aldehyde groups simultaneously in a typical reaction of condensation. It is evident that such an aldehyde should condense with acetone, and that a six-carbon ring should be formed, if both methyl groups were attacked at the same time. Experiment showed that the reaction ran neatly and that in alkaline solution *p*-nitrophenol was formed in satisfactory quantity. The 1-nitro-4-keto-$\Delta_{2,5}$-dihydrobenzol which must be considered to be the first product of the condensation, evidently passes into the *p*-nitrophenol through the addition and elimination of water. The reaction is essentially the same whether the sodium nitromalonic aldehyde is assumed to be the nitro or the isonitro compound, and recalls the removal of the para hydrogens in $\Delta_{2,5}$-dihydrobenzol derivatives by oxidation, as observed by Von Baeyer; or the relation between quinonemonoxime and *p*-nitrosobenzol.

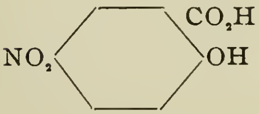


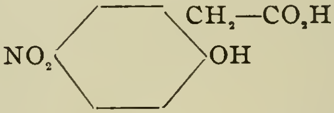


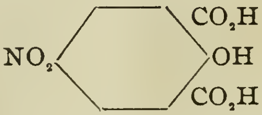
This reaction has been further studied by Messrs. G. Oenslager and C. A. Soch, who have found that a number of ketones and ketone-acids condense readily with nitromalonic aldehyde. From methyl-ethylketone was obtained the nitro-orthocresol of Nevile and Winther[1] melting at 95° while dibenzylketone yielded a nitrophenol derived from *m*-diphenylbenzol. The long-known nitrosalicylic acid melting at 228° was obtained from acetacetic ester, and a derivative of oxyphenylacetic acid of similar structure was made without difficulty from levulinic acid; acetonedicarboxylic acid also gave a nitrooxyisophthalic acid. The mode of condensation was sufficiently confirmed by the formation of the nitrocresol and the nitrosalicylic acid of known constitution, and the several products formed were therefore :











In attempting to prepare the free nitromalonic aldehyde from its sodium salt, we obtained results which confirmed in a striking way our conclusions as to the constitution of the body. When 1 molecule of hydrochloric acid was added to an aqueous solution of the sodium salt, no visible change took place except a slight change of color, but after the lapse of a short time at ordinary temperatures, or more rapidly at a gentle heat, a beautifully crystalline body separated which proved to be symmetrical trinitrobenzol; at the same time formic acid appeared in the solution. It seems probable that the trinitrobenzol is here formed by the spontaneous condensation of nitroacetaldehyde, which is first formed together with formic acid by the addition of water to the nitromalonic aldehyde. The reaction is then precisely analogous to the formation of triacetylbenzol from acetoacetic aldehyde, or of trimesinic acid from malonic aldehyde acid. It is to be noted, however, that the condensation of the similar derivatives of acetaldehyde containing halogens with the formation of the corresponding derivatives of benzol has not been observed, and that it is not impossible, in this case, that the ring formation precedes the elimination of formic acid.

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[1] Ber. d. chem. Ges., 15, 2978.

Nitromalonic Aldehyde.

The sodium salt of nitromalonic aldehyde and its salts with certain other bases were described in 1882 by C. R. Sanger in the preliminary paper already mentioned. As no analytic data were then given, we have thought it best to give here a more extended account of the preparation of the sodium salt which we employed, and to include also the analytical work of Sanger, through which its composition was established.

Sodium Nitromalonic Aldehyde, $NaC_3H_2NO_4.H_2O$.—When mucobromic acid is added to a solution of sodic nitrite in diluted alcohol a vigorous reaction soon sets in, the solution turns deep yellow, then deep red, and at the same time there is a rapid escape of carbonic dioxide. The temperature rises rapidly, and the reaction seems to proceed to best advantage at about 50°. We have usually dissolved 20 grams of sodic nitrite in 50 cc. of water, diluted the solution with an equal volume of alcohol, and then stirred in 20 grams of mucobromic acid. The temperature was allowed to rise spontaneously until it reached 50°. Cooling was seldom necessary to keep it at this point, and, as the reaction slackened, gentle heat was required. As soon as the evolution of carbonic dioxide is over, the solution should be well cooled and vigorously stirred; the solution then solidifies with the separation of finely-felted needles of the sodium salt. The yield is usually 25 per cent of the weight of the mucobromic acid taken, but occasionally it has fallen considerably lower without our being able to fix upon the cause. The crude product is most conveniently purified by recrystallization from somewhat diluted alcohol. The air-dried salt contains 1 molecule of water, which it retains over sulphuric acid; at 100° slow decomposition sets in, so that a direct determination of the water of crystallization is impracticable.

I. 0.5188 gram air-dried salt gave 0.2325 gram Na_2SO_4.

II. 0.5837 gram air-dried salt gave 0.2238 gram Na_2SO_4.

III. 0.2742 gram air-dried salt gave 0.1240 gram Na_2SO_4.

IV. 0.5639 gram air-dried salt gave 0.4788 gram CO_2, and 0.1372 gram H_2O.

V. 0.6526 gram air-dried salt gave 0.5346 gram CO_2, and 0.1617 gram H_2O.

VI. 0.5739 gram air-dried salt gave 0.4883 gram CO_2, and 0.1438 gram H_2O.

VII. 0.5346 gram air-dried salt gave 43.0 cc. moist nitrogen at 26°.5 and under a pressure of 757 mm.

VIII. 0.7758 gram air-dried salt gave 63.5 cc. moist nitrogen at 18°.5 and under a pressure of 750 mm.

	Calculated for	Found.							
	$NaC_3H_2NO_4.H_2O$.	I.	II.	III	IV.	V.	VI.	VII.	VIII.
Na	14.67	14.53	14.41	14.67	....	....	....	....	....
C	22.92	....	....	....	23.16	22.35	23.20	....	....
H	2.56	....	....	....	2.72	2.77	2.77	....	....
N	8.94	....	....	....	....	....	....	8.82	9.26

Sodium nitromalonic aldehyde is very readily soluble in water, but quite sparingly soluble in alcohol; from a hot alcoholic solution it is deposited in long, slender needles. It is not easy to obtain a perfectly colorless salt, although the color appears to be accidental. By treatment with bone-black and repeated recrystallization from alcohol, or by precipitation of the cold alcoholic solution with ether, a white salt may be prepared, but it still gives an aqueous solution, which is faintly tinged with yellow. The material which we have used throughout our work has had a decided reddish-yellow color.

Hill and Sanger did not succeed in isolating the aldehyde itself from the sodium salt, but they made no very persistent efforts in this direction. If an aqueous solution of the salt is acidified with hydrochloric acid and extracted with ether, the ether leaves upon evaporation a viscous oil which usually shows no signs of crystallization on standing. This ethereal extract, however, can easily be shown to contain the aldehyde, since the aniline derivative of the nitromalonic aldehyde melting at 143°–144°, which we shall soon describe, can readily be made from it. The oil dissolves in water, giving a brilliant yellow, clear solution, but this soon grows turbid and deposits a crystalline body which melts, after one recrystallization from alcohol, at 120°–121°. This same crystalline body can be prepared more conveniently by acidifying the solution of the sodium salt with exactly 1 molecule of hydrochloric acid and allowing it to stand. It is formed rapidly at 45°–50°, more slowly, but in somewhat better yield, at ordinary temperatures, while at 0° the formation is extremely slow; at 100° the reaction seems to take, in great part at least, another course. The body was readily soluble in alcohol, ether, chloroform, benzol, and ligroin, but was sparingly soluble even in boiling water. Repeated recrystallization from neutral solvents failed to raise the melting-point above 120°–121°, but after treatment with fuming nitric acid it melted at 121°–122°. This melting-point and the percentage composition of the body identified it as *s*-trinitrobenzol.

I. 0.2676 gram substance gave 0.3334 gram CO_2, and 0.0378 gram H_2O.

II. 0.1008 gram substance gave 17.5 cc. moist nitrogen at 21° and under a pressure of 764 mm.

	Calculated for $C_6H_3(NO_2)_3$.	Found. I.	II.
C	33.78	33.98	....
H	1.42	1.58	....
N	19.76	....	19.79

The body was further identified as *s*-trinitrobenzol through the formation of the characteristic addition-products with benzol and aniline described by Hepp.[1] By dissolving the sodium nitromalonic aldehyde directly in half-normal hydrochloric acid we obtained from 20 to 24 per cent of the theoretical yield of trinitrobenzol, assuming that 3 molecules of the former were needed to form 1 molecule of the latter. A very slight excess of acid diminished the yield greatly; with 2 molecules of acid of this strength hardly any trinitrobenzol was formed.

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[1] Ann. Chem. (Liebig), **215**, 356, 376.

The aqueous solution filtered from the trinitrobenzol proved to contain formic acid in abundance. It was distilled in a current of steam as long as acid was carried over; the acid distillate was boiled with an excess of plumbic carbonate, and the filtered solution concentrated. The lead salt thus obtained had the characteristic appearance of plumbic formate and gave the required percentage of lead.

0.3513 gram of the salt gave 0.3581 gram $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.
Pb	69.69	69.61

In aqueous solution, therefore, nitromalonic aldehyde is decomposed according to the equation:

$$3C_3H_3NO_4 = C_6H_3(NO_2)_3 + 3CH_2O_2.$$

If water is carefully excluded, the nitromalonic aldehyde may be isolated, but its preparation and purification is a matter of some difficulty. If an ethereal solution of hydrochloric acid is added to the silver salt suspended in absolute ether, argentic chloride is at once formed, and the ethereal solution, upon evaporation *in vacuo*, leaves a white crystalline residue, which may be recrystallized from ligroin or from a mixture of ether and ligroin. The analysis of a carefully prepared specimen gave figures which left no doubt as to the identity of the substance, but showed that decomposition had probably already set in.

0.1440 gram substance gave 0.1671 gram CO_2, and 0.0302 gram H_2O.

	Calculated for $C_3H_3NO_4$.	Found.
C	30.80	31.65
H	2.56	2.36

In order to determine whether the aldehyde had gone over into a polymeric form, its molecular weight was determined through the depression of the freezing-point of its benzol solution. 25.1 grams of benzol were employed with the following results:

Substance.	Depression.	Molecular weight.
0.1206	0.200	117.7
0.1299	0.215	118.0

Since these results agree absolutely with the molecular weight 117, calculated from the formula $C_3H_3NO_4$, the substance was the monomolecular form of the aldehyde.

Nitromalonic aldehyde is readily soluble in alcohol, ether, chloroform, or benzol, more sparingly soluble even in boiling ligroin. It may be most conveniently recrystallized from ligroin with the addition of a little ether, and is then obtained in feather-formed aggregations of small, pointed, colorless prisms which melt at 50°–51°. Water dissolves it immediately in the cold, giving an intensely yellow solution which is strongly acid toward litmus or methyl orange. The aqueous solution soon grows turbid with the formation of trinitrobenzol. With aniline it gives the crystalline aniline derivative already mentioned, melting at 143°–144°, and with sodic hydrate it forms the long needles of the sodium salt. It volatilizes rapidly when exposed to the air or even in a desiccator.

Action of Aniline and p-Toluidine.

Nitromalonic Aldehyde Anil, $C_9H_8N_2O_3$.—When aniline hydrochlorate is added to an aqueous solution of the sodic nitromalonic aldehyde, either with or without the addition of free hydrochloric acid, a highly crystalline, bright yellow substance is formed in abundance, which may be purified by recrystallization from alcohol. Analysis showed that it had been formed by the condensation of equal molecules of aniline and the aldehyde with the elimination of water.

I. 0.2202 gram substance gave 0.4543 gram CO_2, and 0.0864 gram H_2O.

II. 0.2453 gram substance gave 0.5045 gram CO_2, and 0.0965 gram H_2O.

III. 0.1202 gram substance gave 15.2 cc. moist nitrogen at 15° and under a pressure of 765 mm.

	Calculated for $C_9H_8N_2O_3$.	Found. I.	II.	III.
C	56.22	56.28	56.10	....
H	4.20	4.39	4.40	....
N	14.62	....	....	14.84

This substance is sparingly soluble in ether, chloroform, benzol, or ligroin, and insoluble in water. It dissolves freely in hot alcohol and crystallizes, as the solution cools, in irregular, lustrous, yellow scales, which melt at 143°–144°. In concentrated sulphuric acid it dissolves readily in the cold and is reprecipitated unchanged on the addition of water. The alkaline hydrates dissolve it at once in the cold, but ether then extracts aniline, and a salt of the aldehyde can be isolated from the solution.

Nitromalonic Aldehyde Dianil, $C_{15}H_{13}N_2O_2$.—If aniline is added to a solution of the sodium salt in water or diluted alcohol, a body is soon thrown down which crystallizes in brilliant yellow needles, while the solution acquires a strongly alkaline reaction. The same body may also be made by the action of aniline in alcoholic solution upon the anil which has just been described. For analysis the substance was recrystallized from dilute alcohol.

I. 0.1716 gram substance gave 0.4224 gram CO_2, and 0.0768 gram H_2O.

II. 0.1494 gram substance gave 19.5 cc. moist nitrogen at 7°.5 and under a pressure of 767 mm.

	Calculated for $C_{15}H_{13}N_3O_2$.	Found. I.	II.
C	67.36	67.14	....
H	4.90	5.01	....
N	15.77	....	15.86

The dianil is more readily soluble in alcohol, ether, chloroform, benzol, or ligroin than the compound with 1 molecule of aniline. As the method of preparation shows, it is little affected by dilute alkaline hydrates, but dilute acids readily convert it into the monoanil. When recrystallized from diluted alcohol it melts at 93°–94°.

Nitromalonic Aldehyde p-Tolil, $C_{10}H_{10}N_2O_3$.—This body is precipitated almost immediately when *p*-toluidine hydrochlorate is added to an aqueous solution of the sodium nitromalonic aldehyde. It closely resembles the corresponding aniline compound in appearance and behavior. When recrystallized from alcohol it melts at 176°–177°.

0.2130 gram substance gave 0.4563 gram CO_2, and 0.0971 gram H_2O.

	Calculated for $C_{10}H_{10}N_2O_3$.	Found.
C	58.21	58.43
H	4.89	5.10

Nitromalonic Aldehyde Di-p-Tolil, $C_{17}H_{17}N_3O_2$.—The ditolil can be made by the action of 2 molecules of toluidine in alcoholic solution upon the sodium salt or upon the monotolil. It closely resembles the dianil, although it is rather more sparingly soluble in the ordinary solvents. When recrystallized from diluted alcohol it melts at 138°. Its composition was established by the following analyses:

I. 0.2071 gram substance gave 0.5278 gram CO_2, and 0.1087 gram H_2O.

II. 0.1590 gram substance gave 19.6 cc. moist nitrogen at 19°.5 and under a pressure of 772 mm.

	Calculated for $C_{17}H_{17}N_3O_2$.	Found. I.	Found. II.
C	69.10	69.52	....
H	5.80	5.87	....
N	14.27	....	14.30

Orthotoluidine gives similar compounds, but they have not been more fully studied. With methylamine, ethylamine, and isoamylamine, bodies may also be obtained which involve 1 or 2 molecules of the amine, and which closely resemble in behavior the aromatic compounds just described.

Action of Phenylhydrazine and of Hydrazine.

The behavior of the nitromalonic aldehyde toward phenylhydrazine demanded careful study, since the formation of pyrazol derivatives might be predicted. We have found that the phenylhydrazones are easily formed, and that they are also readily converted into phenylnitropyrazol.

Nitromalonic Aldehyde Phenylhydrazone, $C_3H_9N_2O_3$.—When 1 molecule of phenylhydrazine hydrochlorate is added to an aqueous solution of sodic nitromalonic aldehyde the hydrazone is soon formed and separates in short, clustered, yellow needles. As the substance could not be recrystallized without danger of decomposition, it was thoroughly washed with cold water, and dried at ordinary temperature. The dried substance had darkened materially in color, and it was therefore washed with a little cold alcohol and again dried. It then gave results on analysis which showed that it was the monohydrazone.

0.2332 gram substance gave 0.4474 gram CO_2, and 0.0958 gram H_2O.

	Calculated for $C_9H_9N_3O_3$.	Found.
C	52.13	52.32
H	4.38	4.59

This hydrazone is slightly soluble in water, and but sparingly soluble in cold ether or alcohol ; it dissolves more freely in hot alcohol, and, if the solution is immediately cooled, small quantities may be recrystallized unchanged. On heating for a few minutes in alcoholic solution, it is converted into phenylnitropyrazol melting at 125°–126° ; the same change is effected even in the cold on long standing. In hot benzol or chloroform the body dissolves freely, more sparingly in the cold ; in carbonic disulphide it is sparingly soluble. On heating the substance melts at about 101°, but again solidifies and melts for a second time at 125°. This ready conversion by heat into the phenylnitropyrazol renders the precise determination of the melting-point impossible. It dissolves readily in dilute sodic hydrate, and phenylhydrazine hydrochlorate yields with this solution the sodium salt of the dihydrazone.

Nitromalonic Aldehyde Diphenylhydrazone, $C_{15}H_{15}N_5O_2$.—Phenylhydrazine dissolved in diluted alcohol reacts upon sodium nitromalonic aldehyde with the elimination of 2 atoms of oxygen ; but since the dihydrazone thus formed is held in solution as a sodium salt, the deep-orange color which the solution soon assumes is the only indication that reaction has taken place. If an acid is now added, a voluminous precipitate of the dihydrazone is thrown down. Since the body is broken up by strong acids with the formation of phenylnitropyrazol, it is better to pass carbonic dioxide into the solution.

An orange-red precipitate at first appears, which grows compact and turns deep-red. As the substance could not be purified by recrystallization, it was washed thoroughly with cold water and carbonic disulphide, and dried over sulphuric acid.

I. 0.1388 gram substance gave 0.3080 gram CO_2 and 0.0649 gram H_2O.

II. 0.1410 gram substance gave 30.0 cc. moist nitrogen at 25° and under a pressure of 761 mm.

	Calculated for $C_{15}H_{15}N_5O_2$.	Found. I.	Found. II.
C	60.54	60.52	....
H	5.08	5.23	....
N	23.61	....	23.94

The dihydrazone is insoluble in water and sparingly soluble in ether, chloroform, carbonic disulphide, benzol, ligroin, or cold alcohol; in hot alcohol it dissolves more freely, but as the solution cools phenylnitropyrazol separates. The formation of the pyrazol derivative is naturally facilitated by the addition of hydrochloric acid. In acetone the body dissolves freely, and is precipitated by the addition of chloroform or carbonic disulphide in a crystalline condition, but the crystals are soon converted into a viscous black mass. By the spontaneous evaporation of the ethereal solution small, deep-red, rhombic plates appear, but no considerable quantities of these crystals could be obtained without decomposition. The body melts at about 98° with decomposition. In alkaline solutions the dihydrazone dissolves freely and forms quite stable salts.

Sodium Nitromalonic Diphenylhydrazone, $NaC_{15}H_{14}N_5O_2$.—If the dihydrazone is dissolved in the requisite amount of half-normal sodic hydrate, the solution soon solidifies on scratching, with the separation of long, finely-felted, yellow needles of the sodium salt. This salt may also be made directly from the sodium nitromalonic aldehyde by the action of an aqueous solution of phenylhydrazine, or from the monohydrazone as already described. The salt is readily soluble in alcohol, sparingly soluble in cold water, more readily in hot, and may be recrystallized from water, if the solution is not too strongly heated.

I. 0.2794 gram salt gave 0.0626 gram Na_2SO_4.

II. 0.1872 gram salt gave 35.5 cc. nitrogen at 22°.5 under a pressure of 764 mm.

	Calculated for $NaC_{15}H_{14}N_5O_2$.	Found. I.	II.
Na	21.99	21.42	....
N	7.22	....	7.27

Lead Nitromalonic Diphenylhydrazone, $Pb(C_{15}H_{14}N_5O_2)_2$.—The yellow-brown lead salt made by double decomposition from the sodium salt was insoluble in water or alcohol.

0.1191 gram of the salt gave 0.0457 gram $PbSO_4$.

	Calculated for $Pb(C_{15}H_{14}N_5O_2)_2$.	Found.
Pb	25.87	26.20

1-Phenyl-4-Nitropyrazol, $C_7H_9N_3O_2$.—The formation of a phenylnitropyrazol from both the phenylhydrazine derivatives of the nitromalonic aldehyde by heating with alcohol has already been mentioned. When recrystallized from alcohol it gave the required percentage composition. The material used in analyses I and III was prepared from the monohydrazone; that used in analysis II was made by the action of dilute hydrochloric acid upon the dihydrazone.

I. 0.2104 gram substance gave 0.4392 gram CO_2, and 0.0732 gram H_2O.

II. 0.2595 gram substance gave 0.5431 gram CO_2, and 0.0908 gram H_2O.

III. 0.1380 gram substance gave 27.2 cc. moist nitrogen at 24°.5 and under a pressure of 765 mm.

	Calculated for $C_9H_7N_3O_2$.	Found. I.	II.	III.
C	57.09	56.96	57.09	....
H	3.73	3.89	3.91	....
N	22.26	....	....	22.10

The 1-phenyl-4-nitropyrazol is readily soluble in ether, chloroform, or benzol, but more sparingly soluble in ligroin. It dissolves readily in hot alcohol and, as the solution cools, it separates in slender clustered prisms, which melt at 126°–127°. It is not easy to remove the accidental color by recrystallization from alcohol, but from ligroin or ether the substance is readily obtained in nearly white, silky needles. It gives without difficulty Knorr's pyrazol reaction. On diluting the alcoholic solution after reduction with sodium, a white crystalline product is thrown down which we have not further examined. While this body had the well-marked character of a pyrazol derivative, it had not previously been described, and it seemed advisable to prepare in a similar way from the nitromalonic aldehyde the 4-nitropyrazol which was first made by Buchner; such a body could evidently be made with the aid of hydrazine.

4-Nitropyrazol, $C_3H_3N_3O_2$.—Hydrazine sulphate gives with an aqueous solution of sodium nitromalonic aldehyde an immediate dark-red precipitate and a similar precipitate is also formed, if one equivalent of sodic carbonate or hydrate is added at the same time; if two equivalents of sodic hydrate are used, a yellow solution is obtained which is slowly precipitated by carbonic dioxide. The dark-red body thrown down in each case proved to be insoluble in all ordinary solvents, and appeared to be analogous to the phenyl compounds already studied. As they interested us mainly in that they might yield the nitropyrazol, we proceeded at once to a study of their decomposition. The product formed by the action of 2 molecules of the hydrazine sulphate with the addition of one equivalent of sodic carbonate proved to be much more stable than the phenylhydrazones. It was little affected by boiling water or alcohol, but when heated with dilute acids it slowly went into solution. On heating with moderately concentrated hydrochloric acid, the decomposition was more rapid; frequently complete solution was soon effected, but occasionally brown-red flocks were formed which resisted the action of the acid. The colorless solution was neutralized with sodic carbonate and extracted with ether. The ethereal solution left on evaporation a white crystalline solid, which was sparingly soluble in cold water, more readily in hot water, readily soluble in alcohol or ether, but sparingly soluble in benzol. It could be most readily purified by recrystallization from dilute alcohol; it could also easily be sublimed between watch-glasses. The recrystallized or resublimed body showed the constant melting-point 157°–158° (162° corrected), and agreed in its properties with the somewhat scanty description of nitropyrazol given by Buchner.[1] For the melting-point of the nitropyrazol Buchner gives 162°, but he does not say whether this is the corrected or the uncorrected temperature. Like the pyrazol of Buchner, this body gives with ammoniacal argentic nitrate a remarkably stable silver derivative. An analysis showed that the substance contained the proper percentage of nitrogen.

0.1146 gram substance gave 37.4 cc. moist nitrogen at 22°.8 and under a pressure of 765 mm.

	Calculated for $C_3H_3N_3O_2$.	Found.
N	37.23	36.92

From the red hydrazine derivative of the nitromalonic aldehyde, therefore, the 4-nitropyrazol is formed by the action of hydrochloric acid. In one case the weight of substance with the proper melting-point amounted to 65 per cent of the theoretical amount. It should be said that a small additional quantity of the nitropyrazol can be extracted by ether from the original mother-liquor from which the dark-red hydrazine compound has been removed by filtration.

Action of Hydroxylamine.

The action of hydroxylamine upon the nitromalonic aldehyde is closely analogous to that of the aromatic amines or hydrazines. In neutral solution hydroxylamine hydrochlorate gives a body which is empirically an anhydride of the monoxime, while in alkaline solution 2 molecules of hydroxylamine enter into reaction, and a salt of the dioxime is formed. The ready decomposition of these bodies has rendered the detailed study of them difficult; a more extended investigation of them is now in progress.

β-Nitroisoxazol, $C_3H_2N_2O_3$.—If 1 molecule of hydroxylamine hydrochlorate is added to a concentrated aqueous solution of sodic nitromalonic aldehyde, a deep-red color is soon developed, and on standing a white crystalline body separates. The same crystalline body is almost immediately obtained in larger quantity, if the hydroxylamine hydrochlorate is added in excess; in this case, however, a yellow instead of a red solution is formed. The crystals which separate may be purified by recrystallization from ligroin, or from a mixture of ether and ligroin. Analysis showed that the body had been formed from the monoxime by the loss of a molecule of water.

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[1] Ann. Chem. (Liebig), 273, 265.

I. 0.2290 gram substance gave 0.2630 gram CO_2, and 0.0375 gram H_2O.

II. 0.2078 gram substance gave 44.8 cc. nitrogen measured over caustic potash at 24° and under a pressure of 763 mm.

	Calculated for $C_3H_2N_2O_3$.	Found. I.	Found. II.
C	31.56	31.33	....
H	1.77	1.83	....
N	24.62	....	24.61

β-Nitroisoxazol is readily soluble in alcohol, ether, benzol, chloroform, sparingly soluble in cold carbonic disulphide, but more readily in hot, and very sparingly soluble even in boiling ligroin. It dissolves sparingly in cold water and gives a colorless solution which is neutral to litmus. The aqueous solution, on standing in the cold, gradually turns yellow and acquires an acid reaction; the same change takes place rapidly on warming. In solutions of the alkaline hydrates it dissolves promptly with the formation of a deep-yellow color; with sodic hydrate ammonia is given off in the cold and hydrocyanic acid is at the same time formed. From the acidified solution ether extracts no well-defined product. When crystallized from a mixture of ether and ligroin it forms clear rhombic plates, which are usually compactly aggregated, and show the constant melting-point, 46°–47°.

Sodium Salt of Nitromalonic Aldehyde Dioxime, $NaC_3H_4N_3O_4$.—When hydroxylamine hydrochlorate is allowed to act in concentrated aqueous solution upon sodium nitromalonic aldehyde with the addition of an equivalent amount of sodic carbonate or sodic hydrate, a sodium salt of the corresponding dioxime gradually separates as a pale-yellow, crystalline precipitate. The salt is rather sparingly soluble in cold water, and the solubility is somewhat increased by heat, but decomposition then soon sets in, and at 100° ammonia and hydrocyanic acid are formed. Evaporation in a desiccator gave us no satisfactory results, and the salt could not be precipitated from aqueous solution by alcohol. We therefore analyzed the carefully prepared salt without further purification.

I. 0.1896 gram air-dried salt gave 0.0814 gram Na_2SO_4.

II. 0.1555 gram air-dried salt gave 33.2 cc. moist nitrogen at 18°.5 and under a pressure of 759 mm.

	Calculated for $NaC_3H_4N_3O_4$.	Found. I.	Found. II.
Na	13.61	13.92	....
N	24.90	....	24.45

This sodium salt crystallizes in clear, yellow, pointed prisms, which are frequently developed in the form of six-sided plates. If sodic hydrate is added to the salt suspended in cold water, it dissolves promptly, and alcohol then precipitates a new sodium salt which has not been further examined. On the addition of hydrochloric acid a complicated reaction takes place, which is at present under investigation, but as yet we have been unable to isolate the dioxime itself. The sodium salt gives with ferric salts a brown-red, with ferrous salts an intense blood-red color, which passes into an equally intense violet on the addition of sodic hydrate; if no large excess of ferrous salt is used, this alkaline solution is clear.

Silver Salt of Nitromalonic Aldehyde Dioxime, $AgC_3H_4N_3O_4$. —The pale-yellow, microcrystalline silver salt was at once precipitated on the addition of argentic nitrate to a solution of the sodium salt, and was not blackened by exposure to diffused light.

0.1000 gram salt gave 0.0566 gram AgCl.

	Calculated for $AgC_3H_4N_3O_4$.	Found.
Ag	42.47	42.60

Nitromalonic Aldehyde Anil-oxime, $C_9H_9N_3O_3$.—If aniline hydrochlorate is added to a solution of the sodium salt of the dioxime, a brilliant yellow, crystalline precipitate is at once thrown down, which can easily be purified by recrystallization from alcohol. Analysis showed that the body had been formed by the replacement of one of the isonitroso groups of the oxime by the phenylimido group.

I. 0.2421 gram substance gave 0.4636 gram CO_2, and 0.0978 gram H_2O.

II. 0.2272 gram substance gave 0.4340 gram CO_2, and 0.0912 gram H_2O.

III. 0.1175 gram substance gave 26.0 cc. moist nitrogen at 18° and under a pressure of 761 mm.

	Calculated for $C_9H_9N_3O_3$.	Found. I.	II.	III.
C	52.12	52.24	52.11	....
H	4.38	4.52	4.50	....
N	20.32	....	....	20.12

This anil-oxime is readily soluble in hot alcohol, and as the solution cools it separates in globular aggregations of yellow crystals which melt at 162°. It is but sparingly soluble in ether, chloroform, or benzol. It dissolves easily in dilute sodic hydrate, and is reprecipitated unchanged by acids. This body may also be made by the action of hydroxylamine upon the nitromalonic aldehyde anil melting at 143°–144°.

Condensation with Acetone.

If sodium nitromalonic aldehyde is dissolved in a small quantity of water, acetone in excess added, and the solution then made alkaline with sodic hydrate, a red color is soon developed which deepens as the solution stands. After the lapse of several hours, solid sodic hydrate is gradually added, and the yellow sodium salt which then separates recrystallized from water. The product which was obtained in this way, when acidified with hydrochloric acid, gave a body crystallizing in long, yellow needles, which melted at 114°. This melting-point and the properties of the substance were sufficient to show that it was *p*-nitrophenol, and the identity of the body was further established by an analysis.

0.1907 gram substance gave 0.3631 gram CO_2, and 0.0650 gram H_2O.

	Calculated for $C_6H_5NO_3$.	Found.
C	51.77	51.93
H	3.62	3.81

In alkaline solution, therefore, the nitromalonic aldehyde and acetone had condensed to form *p*-nitrophenol according to the equation :

$$C_3H_3NO_4 + C_3H_6O = C_6H_5NO_3 + 2H_2O.$$

Similar condensation-products formed from nitromalonic aldehyde by the action of other ketones and ketone acids will be described in a subsequent paper.

CONTRIBUTION TO THE STUDY OF AQUEOUS SOLUTIONS OF DOUBLE SALTS.

III.—CHLORIDES AND BROMIDES.

By Harry C. Jones and Nicholas Knight.

The purpose of this investigation is to study the condition of double chlorides and bromides in the presence of varying amounts of water. These substances are perfectly well-defined compounds, having a composition as definite, and a crystal form as characteristic, as any group of chemical substances.

The question is still unanswered as to the way in which these substances break down in aqueous solution. Are they first decomposed into their constituent molecules, and then these molecules dissociated electrolytically by the water, just as a mixture of the two substances would be, or do the molecules of the double halides exist as such in aqueous solutions, under any conditions?

Considerable work has already been done on this problem. Rüdorff[1] studied the way in which the constituents of double salts diffuse out of a solution of the salt, and divided double salts into two classes, according as their constituents were found in the diffusate in the same proportion as in the double salt, or in a different proportion. The following six double chlorides were found to suffer decomposition in the presence of water:

$2KCl + CuCl_2 + 2H_2O$,
$KCl + MgCl_2 + 6H_2O$,
$2NH_4Cl + CuCl_2 + 2H_2O$,
$2NaCl + CdCl_2 + 3H_2O$,
$2KCl + ZnCl_2 + H_2O$,
$BaCl_2 + CdCl_2 + 4H_2O$.

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[1] Ber. d. chem. Ges., **21**, 4, 1882, 3044.

The following three double chlorides existed as such in the presence of water:

$$2NaCl + PtCl_4 + 8H_2O,$$
$$2KCl + PtCl_2,$$
$$2NH_4Cl + HgCl_2.$$

The first class, according to Rüdorff, are to be regarded as double salts, the second as true molecular binary compounds.

Berthelot,[1] from his thermochemical studies, laid down the general proposition that, "double salts formed with the liberation of a small amount of heat are to be regarded as separated, for the most part, into their constituents, by water." From his work on the double halides of potassium and mercury, he was led to conclude that double salts containing these substances are capable of existing in solution.

Since chemical changes are known to be accompanied by changes in volume, Kremers,[2] finding no change in volume when solutions of salts capable of forming double salts were mixed, concluded that no double salt existed in solution. Groshans,[3] from observations on double chlorides and sulphates, drew the same conclusion.

Grotrian[4] studied the conductivity of the double iodide of potassium and cadmium, and concluded that it was very nearly the sum of the conductivities of the constituents.

The application of the conductivity method to the problem of the existence of double chlorides in solution, has already been made by Jones and Ota.[5] They determined the conductivity of solutions of the double salts:

$$2KCl.ZnCl_2,$$
$$KCl.CdCl_2,$$
$$NaCl.AlCl_3,$$
$$2NH_4Cl.HgCl_2,$$

and then the conductivity of solutions of the constituents, in each case. They then compared the sum of the conductivities of the constituents, with the conductivity of the double salt at the same dilution, and finding that the conductivity of the double salt was always very much less than the sum of the constituents in concentrated solutions, concluded that in such solutions the double salt is only partly broken down into the constituent substances. As the dilution increased, the differences became smaller and finally vanished, showing that in very dilute solutions the double salt was entirely decomposed into its constituents.

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[1] Ann. chim. phys. [5], 29, 198.

[2] Ann. Phys. (Pogg.), 98, 58.

[3] Des Dissolutions aqueuses, 2-7.

[4] Ann. Phys. (Wied.), 18, 177.

[5] This JOURNAL, 22, 5.

We have extended the work which was begun on the double chlorides by Jones and Mackay,[1] and continued by Jones and Ota,[2] to a number of chlorides and bromides, and the results which we have obtained and our conclusions from them are given in this paper. The method of work is essentially the same as that employed by Jones and Ota. The conductivity of the double chloride was studied at various dilutions, then the conductivities of the constituent chlorides at the same dilutions, and the comparisons made as already described.

DOUBLE CHLORIDES.

The compounds of this class which we have studied are:

$2NaCl.ZnCl_2.3H_2O$,
$SrCl_2.2CdCl_2.7H_2O$,
$NH_4Cl.MgCl_2.6H_2O$,
$KCl.MgCl_2.6H_2O$.

The Double Chloride of Sodium and Zinc, $2NaCl.ZnCl_2.3H_2O$.

The sodium chloride and zinc chloride were brought together in the proportion of two equivalents of the former to one of the latter. The double salt crystallizes best when there is a slight excess of zinc chloride present. When an attempt was made to recrystallize the double salt, some sodium chloride first separated. Then the double salt readily crystallized. The double salt crystallizes in thick columns, and we were not able to obtain it in the form of needles, as described in the literature. The salt is deliquescent. Analysis gave the following results:

	Calculated.	Found.
H_2O	17.6	17.9

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[1] This JOURNAL, **19**, 83.

[2] *Ibid.*, **22**, 5.

The zinc in the anhydrous salt was then determined and found to be 25.24 per cent, while the calculated is 25.7 per cent. The solutions of this and of all the following salts were prepared thus: The salt was dissolved in water to approximately the concentration desired. This mother-solution was then standardized by determining some one of the constituents, the one chosen being that which could be most accurately and readily determined. Solutions 2 to 6, and in some cases 2 to 7, were each prepared directly from the mother-solution, by measuring off the desired volume of this solution into a measuring-flask, and then diluting to the required volume. Solutions 6 to 7, and in some cases 7 to 11, were prepared either from 6 or from 7 directly, in the same manner. Then No. 11 was taken as the mother-solution, and the remaining solutions prepared in a similar manner from it. In this way we avoided the accumulative effect of the errors of dilution which result whenever a given solution is diluted a large number of times. Duplicates of every dilution were made and their conductivities determined. All pipettes and measuring flasks used in this work were carefully calibrated by the method of Morse and Blalock.[1] In measuring the conductivity of the solutions two cells were used; one with the electrodes removed some distance from one another for the more concentrated solutions, and the other with the plates close together for the more dilute solutions. This was both more convenient and accurate than to use one cell for all of the dilutions. In this way considerable resistance could be used in the rheostat, even in the most concentrated solutions, and better minima secured; and further, by using the plates close together in the more dilute solutions, the resistance in the rheostat was not so great as to destroy the accuracy of the method.

We used the Ostwald modification of the Kohlrausch method. Two series of conductivity measurements were made, the solutions in each series being prepared separately.

Both cells were carefully standardized with $\frac{n}{50}$ potassium chloride ($\mu_v = 129.7$ at 25°), at the beginning of each series of measurements for every substance employed. All the conductivity measurements were made at 25°.

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[1] This Journal, **16**, 479.

In many cases the most dilute solution with which the wide electrodes were used was placed also in the cell with the electrodes close together, and thus its conductivity determined in both cells. This gave us an extra check on the standardization of both cells.

In the following tables v is the volume of the solution in liters, which contains a gram-molecular weight of the electrolyte. μ_v is the molecular conductivity at volume v.

TABLE I.

Molecular Conductivity of $2NaClZnCl_2$ *(253.3).*

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.14	143.8	143.8	143.8
2.28	209.8	209.8	209.8
3.02	238.7	238.7	238.7
6.04	285.6	285.8	285.7
12.08	320.0	320.2	320.1
24.16	349.1	349.1	349.1
48.32	374.5	374.6	374.5
96.64	391.2	391.2	391.2
193.28	413.5	413.7	413.6
773.12	444.1	446.1	445.1
1546.24	468.3	468.4	468.3
3092.48	480.7	480.9	480.8
6184.96	486.7	488.5	487.6

In each determination of conductivity in the above and following tables, a number of resistances were used in the rheostat. Usually from two to four resistances were employed, the amount of the resistance being so chosen that the readings on the bridge were always between 400 mm. and 600 mm. Thus, each result given, is the average of from two to four conductivity measurements.

For the sake of comparing the conductivities of solutions of sodium zinc chloride, with the sum of the conductivities of the constituents at the same dilutions, we have taken the conductivity measurements of sodium chloride and zinc chloride as determined by Kohlrausch, adding the proper temperature coefficients.

Since there are two molecules of sodium chloride in the double salt to one of zinc chloride, in making the comparison twice the molecular conductivity of sodium chloride at one-half the dilution must be taken.

TABLE II.

Comparison for $2NaCl.ZnCl_2$.

v.	NaCl μ_v 25°.	v.	$ZnCl_2$ μ_v 25°.	Sum.	v.	$2NaCl.ZnCl_2$ μ_v 25°.	Difference.
0.57	153.7	1.14	120.3	274.0	1.14	143.8	130.2
1.14	171.8	2.28	129.8	301.6	2.28	209.8	91.8
1.51	176.4	3.02	130.3	306.7	3.02	238.7	68.0
3.02	185.4	6.04	145.3	330.7	6.04	285.6	45.1
6.04	193.4	12.08	159.5	352.9	12.08	320.1	32.8
12.08	205.4	24.16	179.9	385.3	24.16	349.1	36.2
24.16	211.8	48.32	188.1	399.9	48.32	374.5	25.4
48.32	218.3	96.64	196.2	414.5	96.64	391.2	23.2
96.64	224.2	193.28	213.1	437.3	193.28	413.6	23.7
386.56	230.4	773.12	222.9	453.3	773.12	445.1	8.2
773.12	233.6	1546.24	228.7	462.3	1546.24	468.3	—6.0

The Double Chloride of Ammonium and Magnesium,

$NH_4Cl.MgCl_2.6H_2O$.

The double salt was prepared by bringing together in solution one equivalent of each constituent, and carefully evaporating the solution to crystallization. The salt must be allowed to crystallize slowly, but with proper precaution there is no serious difficulty in obtaining it in pure condition. The salt crystallized in columns. To test the purity of the compound used both water and magnesium were determined.

	Calculated.	Found.
H_2O	42.1	42.5
Mg	9.31	9.14

A solution of the double salt was prepared and carefully standardized by determining the magnesium in a known volume.

TABLE III.

Molecular Conductivity of $NH_4Cl.MgCl_2$ *(148.75).*

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.92	201.8	201.8	201.8
3.84	229.6	229.2	229.4
7.68	252.9	252.9	252.9
15.36	274.8	274.8	274.8
30.72	295.5	295.9	295.7
61.44	312.6	313.2	312.9
122.88	327.4	327.4	327.4
245.76	340.9	340.9	340.9
491.52	349.8	349.8	349.8
983.04	358.5	360.4	359.5
1966.08	369.4	369.5	369.4
3932.16	381.4	380.4	380.9
7864.32	394.9	394.8	394.9

We determined the conductivities of solutions of both of the constituents of this double salt. The ammonium chloride used was the product of the third fractional crystallization of a good sample of the salt. The flame test showed no potassium, and a mere trace of sodium. The chloride was dried to constant weight in an air-bath at 140°, and a standard solution prepared from a weighed quantity of this substance. The magnesium chloride used was prepared by fractional crystallization of a fairly pure specimen of the salt. It was recrystallized twice, when the flame showed that all but a trace of impurities had been removed.

TABLE IV.

Molecular Conductivity of NH_4Cl *(53.49).*

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1	99.3	99.3	99.3
2	104.9	104.9	104.9
4	110.4	110.4	110.4
8	115.8	115.8	115.8
16	120.7	120.9	120.8
40	127.6	127.6	127.6
80	131.8	131.8	131.8
160	134.5	134.0	134.2
320	136.9	136.7	136.8
640	138.0	138.2	138.1
1600	138.9	139.0	138.9

The values which we found for the conductivity of ammonium chloride differed slightly from those obtained by Kohlrausch,[1] our values being somewhat lower in the more concentrated solutions, and a little higher in the more dilute. This difference is probably due to the temperature coefficient which must be added to Kohlrausch's values, to transform them from 18° to 25°. This coefficient is, at best, somewhat uncertain over any considerable range of temperature, and we are therefore inclined to use the values which we found directly at 25°, rather than Kohlrausch's values, to which an uncertain factor must be added.

We measured the conductivity of magnesium chloride directly at 25°, since the conductivity measurements hitherto made with this compound did not meet our requirements. Temperature coefficients are not given for all of the values obtained by Kohlrausch.[2] Vicentini[3] began his work at a dilution of 621 liters, and Walden,[4] who was the only one to work with this substance at 25°, began at a volume of 64 liters. We desired data at much greater concentrations.

TABLE V.

Molecular Conductivity of $MgCl_2$ *(95.26).*

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.76	126.3	126.3	126.3
3.52	143.3	143.3	143.3
7.04	159.8	159.8	159.8
14.08	175.4	174.8	175.1
35.20	190.3	190.3	190.3
70.40	201.1	201.1	201.1
140.8	211.3	211.4	211.3
281.6	221.1	221.1	221.1
563.2	227.4	227.5	227.4
1408.0	234.5	234.5	234.5
2816.0	242.8	243.6	243.2
5632.0	252.5	254.1	253.3
11264.0	260.4	261.6	261.0

Our values for magnesium chloride agree very well with those found by Walden, as far as the two series can be compared.

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[1] Ann. Phys. (Wied.), **26**, 161.

[2] *Loc. cit.*

[3] Atti. d. R. Accad. di Turino, **20**, 1885.

[4] Ztschr. phys. Chem., **2**, 49.

TABLE VI.

Comparison for $NH_4Cl.MgCl_2$.

v.	NH_4Cl. μ_v 25°.	v.	$MgCl_2$. μ_v 25°.	Sum.	v.	$NH_4Cl.MgCl_2$. μ_v 25°.	Difference.
1.92	104.5	1.92	127.9	232.4	1.92	201.8	30.6
3.84	110.0	3.84	144.8	254.8	3.84	229.4	25.4
7.68	115.4	7.68	161.3	276.7	7.68	252.9	23.8
15.36	120.3	15.36	176.3	296.6	15.36	274.8	21.8
30.72	124.7	30.72	186.5	311.2	30.72	295.7	15.5
61.44	129.8	61.44	198.3	328.1	61.44	312.9	15.2
122.88	133.2	122.88	208.7	341.9	122.88	327.4	14.5
245.76	135.7	245.76	218.6	354.3	245.76	340.9	13.4
491.52	137.4	491.52	225.8	363.2	491.52	349.8	13.4
983.04	138.0	983.04	230.2	368.2	983.04	359.5	8.7
1966.08	138.0	1966.08	237.5	375.5	1966.08	369.4	6.1
3932.16	138.0	3932.16	246.6	384.6	3932.16	380.9	3.7
7864.32	138.0	7864.32	257.1	395.1	7864.32	394.9	0.2

The Double Chloride of Potassium and Magnesium, $KCl.MgCl_2.6H_2O$.

One equivalent of potassium chloride was brought in solution with one equivalent of magnesium chloride, and the solution containing the mixture evaporated to crystallization. The double salt did not separate at first, but apparently considerable potassium chloride. After discarding a number of crops of crystals, there appeared well-defined crystals, which were evidently neither of the constituents. These were found, on analysis, to be the double chloride desired.

It is not a simple matter to obtain this salt in quantity. After the double salt began to crystallize the greatest care was necessary in concentrating the solution. To secure enough material for our work (about 100 grams) required nearly four months. Marignac[1] has already described the crystals.

The salt, as in all cases, was carefully dried by pressing between layers of filter-paper. The magnesium was determined with the following result:

	Calculated.	Found.
Mg	8.64	8.63

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[1] Ann. des Mines, [5], **12**, 3.

A solution of the double salt was standardized and the following conductivity measurements made. The conductivity of magnesium chloride had already been determined, and the values for potassium chloride are taken from the results of Kohlrausch.

TABLE VII.

Molecular Conductivity of $KCl.MgCl_2$ *(169.85).*

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.95	196.4	195.2	195.8
3.90	225.9	225.8	225.9
7.80	247.4	247.4	247.4
15.60	270.7	270.7	270.7
31.2	285.4	285.8	285.6
62.4	299.2	299.1	299.1
124.8	313.5	313.6	313.5
249.6	326.5	326.5	326.5
499.2	336.0	336.4	336.2
998.4	345.2	345.2	345.2
1996.8	357.5	358.7	358.1
3993.6	376.5	376.5	376.5
7987.2	394.6	394.7	394.6

The following comparison is made in all respects like the preceding for the double salt of magnesium and ammonium.

TABLE VIII.

Comparison for $KCl.MgCl_2$.

v.	KCl. μ_v 25°.	v.	$MgCl_2$. μ_v 25°.	Sum.	v.	$KCl.MgCl_2$. μ_v 25°.	Difference.
1.95	108.5	1.95	128.2	236.7	1.95	195.8	40.9
3.90	110.1	3.90	145.1	255.2	3.90	225.9	29.3
7.80	115.5	7.80	161.6	277.1	7.80	247.4	29.7
15.60	120.5	15.6	176.5	297.0	15.6	270.7	26.3
31.2	125.4	31.2	186.8	212.2	31.2	285.6	26.6
62.4	127.3	62.4	198.6	325.9	62.4	299.1	26.8
124.8	130.8	124.8	209.0	339.8	124.8	313.5	26.3
249.6	132.3	249.6	218.9	351.2	249.6	326.5	24.7
499.2	133.7	499.2	226.0	359.7	499.2	336.2	23.5
998.4	134.7	998.4	229.3	364.0	998.4	345.2	18.8
1996.8	135.7	1996.8	237.7	373.4	1996.8	358.1	15.3
3993.6	136.1	3993.6	246.8	382.9	3993.6	376.5	6.4
7987.2	136.7	7987.2	257.4	394.1	7987.2	394.6	—0.5

The Double Chloride of Strontium and Cadmium, $SrCl_2.2CdCl_2.7H_2O$.

One equivalent of strontium chloride and two equivalents of cadmium chloride were brought together in solution, and this was evaporated to crystallization. The double salt separated without any serious difficulty, and it was quite a simple matter to obtain the substance in quantity large enough for our work. Both the water and cadmium in the salt were determined.

	Calculated.	Found.
H_2O	19.35	19.36
Cd	34.50	34.20

Von Hauer[1] has already described the crystals.

A standard solution was prepared by determining the cadmium in a measured volume, and from this as a starting-point, the following conductivity measurements were made :

TABLE IX.

Molecular Conductivity of $SrCl_2.2CdCl_2$ *(524.98).*

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
2.18	127.0	126.9	127.0
4.36	184.0	184.1	184.0
8.72	238.5	238.5	238.5
17.44	293.3	293.1	293.2
34.88	348.5	346.5	347.5
69.77	402.1	402.0	402.0
139.52	456.2	456.2	456.2
279.04	506.7	506.8	506.7
558.08	561.5	561.5	561.5
1116.16	613.8	613.7	613.7
2232.32	657.8	657.8	657.8
4464.64	701.5	701.4	701.5
8929.28	739.1	739.0	739.0
17858.56	774.8	774.0	774.4

The conductivity of each of the constituent chlorides was then determined. The measurements which have already been made with strontium chloride were not adequate to our purpose, and the conductivity of cadmium chloride as determined by Grotrian and Wershofen,[2] differed appreciably from the values found by Jones and Ota.[3]

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[1] Sitzungs Bericht. Akad. d. Wissenschaft Wien., **15**, 23; **17**, 331.

[2] Ztschr. phys. Chem., **5**, 431; Ann. Phys. (Wied.), **18**, 177.

[3] This JOURNAL, **22**, 5.

TABLE X.

Molecular Conductivity of $SrCl_2$ *(158.58).*

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1	108.5	108.5	108.5
2	130.1	130.0	130.0
4	146.6	146.6	146.6
8	162.6	162.6	162.6
16	179.4	179.6	179.5
40	196.2	196.0	196.1
80	207.4	207.3	207.4
160	219.0	219.0	219.0
320	229.6	229.0	229.3
640	237.6	237.6	237.6
1600	246.5	246.3	246.4
3200	252.5	252.4	252.5
6400	260.0	260.1	260.0
12800	270.2	270.0	270.1

Our values for the more concentrated solutions are lower than those of Kohlrausch,[1] while for the more dilute we found much greater conductivity than Vicentini.[2] Our values are, however, quite regular, the two series of measurements agreeing well with one another, and the differences between the conductivities as the dilution increases are as regular as could be expected. Furthermore, we were very careful to secure the salt in pure condition by fractional crystallization. The solution was standardized by determining the amount of strontium in a measured volume. The strontium was determined as carbonate. Two determinations of strontium in 5 cc. of the solution gave respectively:

First, 0.7406 gram of strontium carbonate.

Second, 0.7420 gram of strontium carbonate.

The two values are evidently quite concordant. We are unable to find any appreciable source of error in our work with this substance.

As the conductivity of cadmium chloride found by Grotrian and Wershofen differed from that found by Jones and Ota, we determined to repeat the measurements.

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[1] *Loc. cit.*

[2] *Loc. cit.*

TABLE XI.

Conductivity of $CdCl_2$ (183.2).

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
0.932	28.1	28.1	28.1
1.864	44.9	44.9	44.9
3.728	62.8	62.8	62.8
7.456	82.5	82.5	82.5
14.91	101.6	101.4	101.5
37.375	129.5	129.6	129.6
74.75	150.3	150.3	150.3
149.50	171.7	171.7	171.7
299.0	192.2	192.4	192.3
598.0	206.6	206.4	206.5
1495.0	227.7	227.6	227.6
2990.0	242.0	241.9	242.6
5980.0	255.3	255.3	255.3

Our values for cadmium chloride agree very satisfactorily with those obtained by Jones and Ota, and therefore differ quite appreciably from the results found by Grotrian and Wershofen.

TABLE XII.

Comparison for $SrCl_2.2CdCl_2$.

v.	$SrCl_2$. μ_v 25°.	v.	$CdCl_2$. μ_v 25°.	Sum.	v.	$SrCl_2.2CdCl_2$. μ_v 25°.	Difference.
2.18	131.5	1.09	61.9	193.4	2.18	127.0	66.4
4.36	148.1	2.18	94.3	242.4	4.36	184.0	58.4
8.72	164.4	4.36	132.2	296.6	8.72	238.5	58.9
17.44	180.5	8.72	171.6	352.1	17.44	293.2	58.1
34.88	192.6	17.44	209.4	402.0	34.88	347.5	54.5
69.76	204.6	34.88	252.5	457.1	69.76	402.0	55.1
139.5	216.8	69.76	295.1	511.9	139.5	456.0	55.9
279.0	224.5	139.5	337.5	562.0	279.0	506.7	55.3
558.1	235.6	279.0	379.0	614.6	558.1	561.5	53.1
1116.2	242.0	558.1	409.2	651.2	1116.1	613.7	37.5
2232.4	248.6	1116.2	436.1	684.7	2232.4	657.8	26.9
4464.8	258.3	2232.4	464.8	723.1	4464.8	701.5	21.6
8929.6	264.1	4464.8	496.7	760.8	8929.6	739.1	21.7

Discussion of the Results Obtained with Double Chlorides.

The problem, as already stated, is to determine whether these double chlorides exist to any extent as such in the solutions, or break down completely into their constituents? If the latter is true, then the " difference" will either be zero if the solutions are isohydric," or it will have a small value if the solutions are not isohydric. If, on the contrary, the double salt exists to any appreciable extent in the solution, the value of the "difference" will be greater. In examining the results the point of direct interest is to examine the magnitude of what we have tabulated under the head of " difference." The first salt studied, *i. e.* the double chloride of sodium and zinc, shows unusually large differences in the concentrated solutions; indeed, larger differences throughout than was found by Jones and Mackay, and later by Jones and Ota[1] for the corresponding potassium zinc chloride. These differences diminish rapidly with increase in dilution, disappearing at a dilution of 500 to 600 liters. It seems strange that the sodium salt should show much larger differences than the potassium, but this is the case.

The values of the differences for the two double chlorides, potassium magnesium, and ammonium magnesium, are much less than for the salt just considered. Yet they are very appreciable. They are of about the same order of magnitude for the two salts, being somewhat greater throughout for the potassium than for the ammonium compound. These differences disappear in both cases in the more dilute solutions.

The differences for the double chloride of cadmium and strontium are much larger than for the magnesium salts, but much smaller than for the sodium zinc bromide. Furthermore, the differences in this case decrease much more slowly with increase in dilution than in any of the preceding salts. This shows that the double chloride of strontium and cadmium is capable of existing, to some extent, at greater dilution than any of the salts thus far studied.

Before any final conclusion can be drawn with reference to the condition of the double salts in solution, we must determine what effect the presence of one of the constituent chlorides has on the dissociation of the other chloride. It is well known that in solutions which are not isohydric, the presence of a substance with a common ion will drive back the dissociation of another substance. It might be possible that our differences are entirely or partially produced in this way, the conductivity of the double salt being less than the sum of the conductivities of the constituents, because each constituent drives back the dissociation of the other to some extent, and thus diminishes the conductivity of solutions of the double salt.

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[1] *Loc. cit.*

It is very important that the amount by which one chloride diminishes the conductivity of another should be determined by direct experiment. We could then see whether our "differences" are due to the action of one of the constituent chlorides on the conductivity of the other, or to the presence of a certain amount of the double salt in solution.

We have tried to settle this point experimentally, as follows: Two chlorides which could not form a double salt with one another were mixed in definite quantities, and the conductivity of the solution determined. Then the conductivity of each chloride was ascertained, separately, at the same dilution. The sum of the conductivities of the solutions of the single chlorides was then subtracted from the conductivity of the mixture at the same dilution. The resulting difference would necessarily be an expression of the sum of the effect of each chloride on the dissociation of the other.

Mixtures of Chlorides Which Do Not Form a Double Salt.

We chose potassium chloride and ammonium chloride as compounds which do not form double salts with one another. These were taken because they could be easily obtained in pure condition; indeed, we had already prepared pure specimens of both substances. We mixed a gram-molecular weight of potassium chloride with a gram-molecular weight of ammonium chloride, and dissolved the mixture to a liter of solution. This was used as the mother-solution for all the remaining dilutions. The conductivities of these solutions are given in the following table:

TABLE XIII.

Conductivities of Mixtures of $KCl + NH_4Cl$.

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1	179.3	179.3	179.3
2	195.0	195.1	195.0
4	208.2	208.4	208.3
8	220.9	221.0	220.9
16	231.7	231.7	231.7
32	241.1	241.3	241.2
40	245.8	246.0	245.9
80	254.2	254.4	254.3
160	262.6	262.0	262.3
320	267.0	267.0	267.0
640	273.1	273.1	273.1
1600	279.2	279.0	279.1

TABLE XIV.

Comparison for $KCl.NH_4Cl$.

v.	KCl. μ_v 25°.	v.	NH_4Cl. μ_v 25°.	Sum.	v.	$KCl.NH_4Cl$. μ_v 25°.	Difference.
1	104.1	1	99.3	203.4	1	179.3	24.1
2	108.6	2	104.9	213.5	2	195.0	18.5
4	111.2	4	110.4	221.6	4	208.3	13.3
8	116.5	8	115.8	232.3	8	220.9	11.4
16	121.5	16	120.9	242.4	16	231.7	10.7
32	125.4	32	125.3	250.7	32	241.2	9.5
40	125.7	40	127.6	253.3	40	245.9	7.4
80	128.5	80	131.8	260.3	80	254.3	6.0
160	131.1	160	134.2	265.3	160	262.3	3.0
320	132.1	320	136.8	268.9	320	267.0	1.9
640	133.9	640	138.1	272.0	640	273.1	—1.1
1600	135.4	1600	138.9	274.3	1600	279.1	—4.8

A mixture was then prepared containing one equivalent of potassium chloride and two of ammonium chloride, and studied in exactly the same manner as the above mixture. This was done for the purpose of determining the effect when one of the constituents was in excess. The following results were obtained :

TABLE XV.

Conductivities of Mixtures of $KCl.2NH_4Cl$.

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1	251.5	251.5	251.5
2	278.5	278.1	278.3
4	301.1	302.1	301.5
8	322.4	322.8	322.6
16	340.8	340.8	340.8
32	353.1	353.9	353.5
40	362.8	362.9	362.8
80	376.5	376.5	376.5
160	390.1	390.7	390.4
320	400.1	400.3	400.2
640	410.6	410.6	410.6
1600	414.1	415.7	414.9

TABLE XVI.

Comparison for $KCl.2NH_4Cl$.

v.	KCl. μ_v 25°.	v.	NH_4Cl. $2\mu_v$ 25°.	Sum.	v.	$KCl.2NH_4Cl$. μ_v 25°.	Difference.
1	104.1	0.5	188.6	292.7	1	251.5	41.2
2	108.6	1	198.6	307.2	2	278.3	28.9
4	111.2	2	209.8	321.0	4	301.5	19.5
8	116.5	4	220.8	337.3	8	322.6	14.7
16	121.5	8	231.6	353.1	16	340.8	12.3
32	125.4	16	241.8	367.2	32	353.5	13.7
40	125.7	20	244.0	369.7	40	362.8	6.9
80	128.5	40	255.2	383.7	80	376.5	7.2
160	131.1	80	263.6	394.7	160	390.4	4.3
320	132.1	160	268.4	400.5	320	400.2	0.3
640	133.9	320	273.6	407.5	640	410.6	—3.1
1600	135.4	640	277.8	413.2	1600	414.9	—1.7

If we compare the differences with these mixtures which cannot form double salts, with the differences for the double salts, we are forced to the following conclusions: The mixture of 1 molecule of potassium chloride with 1 molecule of ammonium chloride, must be compared with the double salts containing 1 molecule of each chloride, in this case with potassium magnesium, and ammonium magnesium chlorides. The differences for the double salts are much larger than for the mixture, in the more concentrated solutions, and persist to much greater dilutions. Thus, the difference entirely disappears in the mixture at about 500 liters, but does not disappear in the double salts until a dilution of several thousand liters is reached.

Comparing the differences for the mixture of 1 molecule of potassium chloride and 2 molecules of ammonium chloride, with those for the double chlorides containing 1 molecule of one chloride and 2 molecules of the other, the following relations appear. The differences for sodium zinc chloride are much greater than for the mixture, and persist at greater dilution. The differences for strontium cadmium chloride are not only much greater than for the mixture, at the same dilutions, but are very much more persistent, not disappearing at the greatest dilution with which we worked,—nearly 9,000 liters.

We seem then to be forced to the conclusion, that all four of these double chlorides exist, to a considerable extent, in the more concentrated solutions, and are broken down completely by water only at very high dilutions. This is the same conclusion as that reached by Jones and Ota[1] through their study of a number of double chlorides. But since they did not study mixtures of chlorides incapable of forming double salts, their conclusion was not based upon evidence as complete as that now at our disposal.

Freezing-point Lowering Produced by Double Chlorides.

Jones and Mackay[2] employed not only the conductivity method to throw light on the condition of double sulphates in solution, but also the freezing-point method. Jones and Ota[3] also attempted to apply the freezing-point method to the problem of double chlorides in solution, but as they were unable to obtain satisfactory results, they did not publish them.

Not content with the experience of Jones and Ota in this direction, we again attempted to apply the freezing-point method to the problem of the double chlorides. We first studied the freezing-point lowering of three of the double chlorides already investigated by the conductivity method. These were ammonium magnesium chloride, sodium zinc chloride, and strontium cadmium chloride. Below are given the volumes of the solutions used, and the molecular lowerings found at these volumes.

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[1] *Loc. cit.* [2] *Loc. cit.* [3] *Loc. cit.*

TABLE XVII.

Freezing-point Lowering of Double Chlorides.

$NH_4Cl.MgCl_2$.		$2NaCl.ZnCl_2$.		$SrCl_2.2CdCl_2$.	
Volume.	Molecular lowering.	Volume.	Molecular lowering.	Volume.	Molecular lowering.
1.92	9.48	3.03	12.27	2.18	9.31
3.84	8.71	6.06	11.84	4.36	9.83
7.68	8.52	12.12	11.71	8.72	10.51
15.36	8.63	24.24	11.84	17.44	11.18
30.72	8.89	48.48	12.47	34.88	11.90
61.44	9.31			69.76	12.67
122.88	9.65				

The molecular lowering of strontium cadmium chloride is regular, *i. e.*, increases throughout with increase in dilution. But the molecular lowerings of sodium zinc, and ammonium magnesium chlorides, are greater in the more concentrated solutions, decrease with increase in dilution to a minimum, and then increase from this point as the dilution increases. That there should be a minimum in the curve expressing the relation between concentration and molecular lowering is, of course, abnormal, and excluded the use of this method for the purpose of throwing light on the problem under investigation.

The freezing-point lowering of one of the constituents, magnesium chloride, was, however, determined. This had been found by Loomis[1] to give results of the same general character as those which we found for two of the double chlorides. The freezing-point curves showed a decided minimum. The results which we obtained for magnesium chloride are given in the following table :

TABLE XVIII.

Freezing-point Lowerings of $MgCl_2$.

Volume.	Molecular lowering.
1.76	5.70
3.52	5.14
7.04	4.88
14.08	4.98
28.16	5.30

[1] Ann. Phys. (Wied.), 57, 503.

Here again was clear evidence of a minimum in the freezing-point curve. We did not carry our work further in this direction. The problem of the freezing-point lowering of a number of single chlorides has since been taken up in this laboratory by Mr. V. J. Chambers. The results of his investigation will soon be published in this JOURNAL. It may be stated in advance that a minimum in the molecular lowering has been found for a number of chlorides and bromides, and we have a theory which we think will account for these apparently abnormal results.

Jones and Ota determined the freezing-point lowerings of the four double chlorides which they investigated. As their results have never been published they will now be given.

TABLE XIX.

Molecular lowering $2KCl.ZnCl_2$.		Molecular lowering $KCl.CdCl_2$.	
Volume.	Molecular lowering.	Volume.	Molecular lowering.
2	12.12	2	5.21
4	12.05	4	5.81
8	12.27	8	6.37
16	12.49	16	7.07
32	13.00	32	7.90
64	13.10	64	8.44
128	13.12	128	9.21

TABLE XX.

Molecular lowering $NaCl.AlCl_3$.				Mol. lowering $2NH_4Cl.HgCl_2$.	
Volume.	First series.	Volume.	Second series.	Volume.	Molecular lowering.
4.21	10.04	5.76	10.14	10	6.97
8.42	10.12	11.53	10.00	15	7.33
16.84	10.44	23.06	10.49	20	7.70
33.68	10.65	46.12	10.67	30	7.86
67.36	10.78	92.24	10.76		
134.72	11.04	184.48	10.86		

In neither of these four cases, with the possible exception of the first, is there any evidence of a minimum in the molecular lowering.

It is clear, from what has already been stated, that no light can be thrown on the nature of double chlorides in solution by the freezing-point method. We must be content with the evidence from the conductivity method alone.

DOUBLE BROMIDES.

The double bromides which we have studied are:

$BaBr_2.CdBr_2.4H_2O$,
$KBr.CdBr_2.\frac{1}{2}H_2O$,
$2NaBr.3CdBr_2.6H_2O$,
$3NH_4Br.ZnBr_2$.

These have been dealt with in exactly the same manner as the double chlorides. The conductivity of each constituent has been determined, then the conductivity of the double salt, and the sum of the former compared with the latter.

The Double Bromide of Barium and Cadmium, $BaBr_2.CdBr_2.4H_2O$.

The constituent bromides were brought together in equivalent quantities, and then a slight excess of cadmium bromide added. The double salt crystallizes from this mixture in thick columns. The salt was analyzed both for water and cadmium with the following results:

	Calculated.	Found.
H_2O	11.22	11.52
Cd	17.5	17.2

TABLE XXI.

Molecular Conductivity of $BaBr_2.CdBr_2$ *(569.55).*

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.97	126.0	126.1	126.0
3.94	166.0	166.0	166.0
7.88	205.9	205.5	205.7
15.76	243.7	243.8	243.7
31.52	276.6	276.7	276.6
63.04	309.7	309.7	309.7
78.08	324.0	324.8	324.4
156.16	357.7	357.7	357.7
312.32	392.4	392.4	392.4
624.64	428.0	429.0	428.5
1249.28	457.9	457.9	457.9
2498.56	481.9	481.7	481.8
3112.20	493.5	493.4	493.5
6226.40	518.9	519.0	518.9

We determined the conductivities of both constituent bromides, directly, at 25°. A solution of purified barium bromide was standardized and made the mother-solution for all the subsequent dilutions.

TABLE XXII.

Molecular Conductivity of $BaBr_2$ *(297.34).*

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
2	147.7	147.6	147.7
4	162.4	162.4	162.4
8	176.4	176.6	176.5
16	190.9	190.9	190.9
32	202.0	202.1	202.0
80	218.5	218.5	218.5
160	228.7	228.9	228.8
320	241.5	241.5	241.5
640	249.2	249.2	249.2
1280	257.1	257.2	257.1
3200	270.7	270.9	270.8
6400	280.8	280.8	280.8

A solution of purified cadmium bromide was standardized by determining the amount of cadmium oxide in a measured volume. From this all the remaining dilutions were made in the manner already described.

TABLE XXIII.

Molecular Conductivity of $CdBr_2$ *(272.21).*

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
2.60	41.3	41.3	41.3
5.20	57.4	57.4	57.4
10.40	75.7	75.7	75.7
20.80	95.0	95.2	95.1
41.60	115.3	115.4	115.3
104.0	144.1	144.3	144.2
208.0	166.1	166.0	166.0
416.0	188.9	188.7	188.8
832.0	209.3	209.3	209.3
1664.0	228.3	228.2	228.2
3328.0	242.5	242.3	242.4
6656.0	256.3	256.0	256.1

Since there is one molecule of barium bromide to one of cadmium bromide in the molecule of the double salt, the comparison is made by taking the sum of the constituents at the same dilution, and comparing this with the conductivity of the double salt at the same dilution.

TABLE XXIV.

Comparison for $BaBr_2.CdBr_2$.

v.	$BaBr_2$. μ_v 25°.	v.	$CdBr_2$. μ_v 25°.	Sum.	v.	$BaBr_2.CdBr_2$. μ_v 25°.	Difference.
1.97	147.5	1.97	37.3	184.8	1.97	126.0	58.8
3.94	162.0	3.94	49.7	211.7	3.94	166.0	45.7
7.88	176.1	7.88	66.6	242.7	7.88	205.7	37.0
15.76	190.1	15.76	85.4	275.5	15.76	243.7	31.8
31.52	201.7	31.52	105.2	306.9	31.52	276.6	30.3
63.04	212.0	63.04	125.0	337.0	63.04	309.7	27.3
78.08	218.2	78.08	132.3	350.5	78.08	324.4	26.1
156.16	228.1	156.16	155.3	383.4	156.16	357.7	25.7
312.32	240.8	312.32	177.4	418.2	312.32	392.4	25.8
624.64	248.9	624.64	199.0	447.9	624.64	428.5	19.4
1249.28	256.9	1249.28	218.8	475.7	1249.28	457.9	17.8
2498.56	264.2	2498.56	235.3	499.5	2498.56	481.8	17.7
3113.2	270.0	3113.2	241.0	511.0	3113.2	493.5	17.5
6226.4	280.1	6226.4	255.0	535.1	6226.4	518.9	16.2

The Double Bromide of Potassium and Cadmium, $KBr.CdBr_2.\frac{1}{2}H_2O$.

To prepare the salt, one equivalent of potassium bromide was brought together with one equivalent of cadmium bromide. The salt was easily obtained in such quantity as we desired for our work. The cadmium in the salt was determined:

	Calculated.	Found.
Cd	28.04	27.76

We also determined the conductivity of solutions of potassium bromide using volumes ranging from 0.981 to 3140. The conductivity determinations hitherto made with this substance by Kohlrausch,[1] Ostwald,[2] and Krannhals[3] did not cover the range of dilution desired.

TABLE XXV.

Molecular Conductivity of $KBr.CdBr_2$*(391.3).*

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
0.938	76.0	76.0	76.0
1.876	95.8	95.7	95.8
3.75	122.7	122.7	122.7
7.50	150.3	150.1	150.2
15.0	177.2	177.2	177.2
30.0	201.5	201.7	201.6
37.5	213.8	213.7	213.8
75.0	240.5	240.5	240.5
150.0	266.7	266.7	266.7
300.0	294.0	294.1	294.0
600.0	319.1	319.1	319.1
1200.0	342.1	342.4	342.2
1500.0	351.2	351.4	351.3
3000.0	370.7	370.7	370.7
6000.0	387.8	388.0	387.9

TABLE XXVI.

Molecular Conductivity of KBr*(119.09).*

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
0.981	104.1	104.1	104.1
1.962	111.0	110.9	111.0
3.924	116.9	116.9	116.9
7.848	122.3	122.3	122.3
15.696	126.4	126.4	126.4
39.24	131.4	131.5	131.4
78.48	134.5	134.3	134.4
156.96	137.1	137.3	137.2
314.0	140.0	139.9	140.0
628.0	142.6	142.6	142.6
1256.0	145.1	145.1	145.1
1570.0	146.0	146.0	146.0
3140.0	146.7	146.7	146.7

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[1] Ann. Phys. (Wied.), 6, 1.

[2] Ztschr. phys. Chem., 1, 74.

[3] *Ibid.*, 5, 250.

TABLE XXVII.

Comparison for $KBr.CdBr_2$.

v.	KBr. μ_v 25°.	v.	$CdBr_2$. μ_v 25°.	Sum.	v.	KBr. $CdBr_2$. μ_v 25°.	Difference.
0.938	103.5	....		....	0.938	76.0	...
1.876	110.8	....		....	1.876	95.8	...
3.750	116.4	3.75	48.4	164.8	3.75	122.7	42.1
7.50	121.8	7.50	65.5	187.3	7.50	150.2	37.1
15.0	126.0	15.0	84.3	210.3	15.0	177.2	33.1
30.0	129.4	30.0	104.1	233.5	30.0	201.6	31.9
37.5	131.0	37.5	111.3	242.3	37.5	213.8	28.5
75.0	134.2	75.0	130.7	264.9	75.0	240.5	24.4
150.0	136.9	150.0	153.9	290.8	150.0	266.7	24.1
300.0	139.7	300.0	176.1	315.8	300.0	294.0	21.8
600.0	142.4	600.0	197.9	340.3	600.0	319.1	21.2
1200.0	144.9	1200.0	217.8	362.7	1200.0	342.2	20.5
1500.0	146.8	1500.0	224.6	371.4	1500.0	351.3	20.1
3000.0	146.7	3000.0	242.4	389.1	3000.0	370.7	18.4
6000.0	147.0	6000.0	256.0	403.0	6000.0	387.9	15.1

A New Double Bromide of Sodium and Cadmium,
$2NaBr.3CdBr_2.6H_2O$.

We brought the constituent bromides together in the proportion to form the double salt, $2NaBr.2CdBr_2.5H_2O$, which is described in the literature. A beautifully crystallized salt separated in plates, and was supposed to be the one described. The cadmium in the double salt was determined.

	Found.	
	I.	II.
Cd	30.0	29.6

The water was determined by drying a weighed portion of the salt to constant weight at 160°.

	Found.	
	I.	II.
H_2O	10.5	10.3

The bromine was then determined.

	Found.	
	I.	II.
Br	56.47	56.63

The cadmium, water, and bromine, correspond to a salt having the composition expressed by the formula:

$$2NaBr.3CdBr_2.6H_2O.$$

	Calculated.
Cd	29.8
H_2O	9.55
Br	56.59

A solution of the double salt was prepared and standardized, by determining the amount of cadmium in a known volume of the solution. From this standardized solution all the remaining dilutions were prepared. The conductivity of sodium bromide was determined over the range of dilutions desired. That of cadmium bromide had already been determined.

TABLE XXVIII.

Molecular Conductivity of $2NaBr.3CdBr_2$ *(1022.63).*

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
2.443	132.8	132.4	132.6
4.886	187.4	187.6	187.5
9.772	248.0	248.2	248.1
19.544	315.9	316.0	315.9
39.088	387.0	387.0	387.0
78.176	457.7	457.8	457.7
97.72	478.3	478.3	478.3
195.44	548.3	548.3	548.3
390.88	625.1	625.5	625.3
781.76	701.6	701.6	701.6
1563.52	780.0	781.6	780.8
3908.80	856.0	857.5	856.8
7817.6	910.7	910.7	910.7
15635.2	958.5	962.4	960.4

TABLE XXIX.

Molecular Conductivity of NaBr(103.0).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1	80.6	80.0	80.3
2	88.0	88.0	88.0
4	94.4	94.4	94.4
8	100.6	101.0	100.8
16	105.3	105.3	105.3
40	110.6	111.1	110.8
80	113.1	113.1	113.1
160	116.6	116.6	116.6
320	119.0	119.4	119.2
640	120.9	120.9	120.9
1600	121.1	121.2	121.1

In comparing the conductivity of the double salt with the sum of the conductivities of the constituents, twice the molecular conductivity of sodium bromide at one-half the dilution of the double salt is taken. To this is added three times the molecular conductivity of cadmium bromide at one-third the dilution of the double salt. The reason for this is apparent from the composition of the double salt.

TABLE XXX.

Comparison for $2NaBr.3CdBr_2$.

Volume.	NaBr. $2\mu_v$ 25°.	Volume.	$CdBr_2$. $3\mu_v$ 25°.	Sum.	Volume.	2NaBr. $3CdBr_2$. μ_v 25°.	Difference.
2.443	179.5	1.63	90.9	270.4	4.88	187.5	82.9
4.886	189.6	3.26	135.9	325.5	9.77	248.1	77.4
9.772	203.6	6.51	185.7	389.3	19.54	315.9	73.4
19.544	212.0	13.03	241.1	453.1	39.09	387.0	66.1
39.088	220.8	26.06	300.0	520.8	78.18	457.7	63.1
48.86	222.6	32.6	318.1	540.7	97.72	478.3	62.4
97.72	227.8	65.1	383.1	610.9	195.44	548.3	62.6
195.44	234.6	130.3	448.1	682.7	390.88	625.3	57.4
390.88	239.6	260.6	515.4	755.0	781.76	701.6	53.4
781.76	242.0	521.2	591.7	833.7	1563.52	780.8	52.9
1563.53	242.4	1302.9	657.9	900.3	3908.8	856.8	43.5
3908.8	242.5	2605.9	705.0	947.5	7817.6	910.7	37.8
7817.6	242.5	5211.7	750.9	993.4	15635.2	960.4	33.0

A New Double Bromide of Ammonium and Zinc, $3NH_4Br.ZnBr_2$.

The constituent bromides were brought together in the proportion to form the double bromide, $2NH_4Br.ZnBr_2$, as described. After about two months 100 grams of a well-crystallized salt were obtained, and this was analyzed. One analysis showed the salt to contain 12.8 per cent of zinc, and a second analysis gave 12.6 per cent. The percentage of zinc in the salt $2NH_4Br.ZnBr_2.H_2O$, is 14.9. We concluded that either there was present a second double salt containing more than 2 molecules of ammonium bromide to 1 of zinc bromide, or that some ammonium bromide had crystallized out along with the double salt. A careful examination of the crystals showed that some were apparently of different habit from the remainder, being relatively much longer. It therefore seemed probable that we were dealing with a mixture.

The attempt was then made to recrystallize the salt. We were, however, unable to obtain it a second time, until a large quantity of a solution of the mixture $2NH_4Br.ZnBr_2$ was added. The salt crystallized readily out of this mixture, but again in both the longer and shorter crystals. The longer crystals were now separated mechanically from the shorter, and analyzed.

	Calculated for $3NH_4Br.ZnBr_2$.	Found.	
		Longer crystals.	Shorter crystals.
Zn	12.6	12.8	12.5

To determine whether the salt contained water of crystallization, 3.4428 grams were heated for four hours in an air-bath, at 130°. The loss was 0.9 per cent. The salt was then further heated for four hours at 160°, when a slight decomposition took place. The total loss in weight amounted to only 1 per cent. It was therefore concluded that the salt contained no water of crystallization, the slight loss in weight observed being due to water which could not be removed by drying-paper, on account of the hygroscopic nature of the salt.

The bromine in the salt was then determined by two analyses, and found to be 77.24 per cent. The bromine calculated for $3NH_4Br.ZnBr_2$ is 77.01 per cent.

A standard solution of the salt was prepared by determining the zinc in a measured volume of the mother-solution.

TABLE XXXI.

Conductivity of $3NH_4Br.ZnBr_2$(519.37).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.623	280.1	280.5	280.3
3.246	367.2	367.2	367.2
6.492	417.0	418.1	417.5
12.984	458.9	459.0	458.9
25.968	496.1	496.2	496.1
51.93	518.6	518.6	518.6
64.92	524.9	524.9	524.9
129.84	552.0	553.0	552.5
259.68	570.8	570.9	570.8
519.36	596.4	596.8	596.6
1038.72	621.7	621.8	621.7
2077.4	641.9	641.9	641.9
2596.8	651.0	651.1	651.0
5193.6	675.9	675.9	675.9

The molecular conductivity of ammonium bromide was determined, with a specimen which had been repeatedly crystallized, starting with a large quantity of fairly pure salt.

TABLE XXXII.

Molecular Conductivity of NH_4Br *(98.02).*

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
0.92	100.0	100.0	100.0
1.84	106.0	106.1	106.0
3.68	111.4	111.2	111.3
7.36	117.3	117.3	117.3
14.72	121.8	122.0	121.9
36.8	127.9	127.7	127.8
73.6	130.9	131.0	130.9
147.2	133.9	133.9	133.9
294.5	137.0	137.3	137.1
588.8	139.7	139.6	139.6
1472.0	141.3	141.1	141.2

The conductivity of zinc bromide in water could not be determined directly, since the bromide is so readily decomposed by water. By comparing a number of chlorides and bromides we find the conductivity of the latter to be about 2 units greater than the former, for equal concentrations. To obtain the conductivity of zinc bromide at any dilution, we have taken the conductivity of zinc chloride at that dilution and added 2 units. This is, of course, only approximate, but is the best that can be done under the conditions. This could not be done, even approximately, for cadmium bromide, since it is well known that the cadmium halides show abnormally small dissociation, and this decreases very rapidly from the chloride to the iodide. While this same phenomenon begins to manifest itself with zinc, yet it is very much less pronounced than with cadmium. The error in the conductivity of zinc bromide, as calculated above, cannot be very great.

TABLE XXXIII.

Comparison for $3NH_4Br.ZnBr_2$.

v.	NH_4Br. $3\mu_v$ 25°.	v.	$ZnBr_2$. μ_v 25°.	Sum.	v.	$3NH_4Br.ZnBr_2$. μ_v 25°.	Difference.
0.541	285.0	1.623	80.0	365.0	1.623	280.3	84.7
1.082	303.0	3.246	132.5	435.5	3.246	367.2	68.3
2.164	321.3	6.492	148.4	469.7	6.492	417.5	52.2
4.328	337.2	12.984	164.2	501.4	12.984	458.9	42.5
8.656	354.3	25.968	183.9	538.2	25.968	496.1	42.1
21.64	371.4	64.92	192.7	564.1	64.92	524.9	39.2
43.28	385.5	129.84	206.6	592.1	129.84	552.5	39.6
86.56	393.9	259.68	216.6	610.5	259.68	570.8	39.7
173.13	399.0	519.36	222.6	621.6	519.36	596.6	25.0
346.24	411.0	1038.72	226.1	637.1	1038.72	621.7	15.4
865.6	420.0	2596.8	234.5	654.5	2596.8	651.0	3.5
1731.1	423.9	5193.6	237.0	670.9	5193.6	675.9	—5.0

Discussion of the Results Obtained with Double Bromides.

Examining the results obtained with the double bromides as with the double chlorides, the chief point of interest is the magnitude of the "differences" found. These are quite large in the concentrated solutions of barium cadmium bromide, and diminish slowly with increase in dilution. They do not disappear even at a dilution of 6,000 liters. This is strictly analogous to what was observed in the case of the double chloride of strontium and cadmium, the differences persisting in greater dilutions of this chloride than in either of the other double chlorides studied.

The differences for potassium cadmium bromide are almost exactly of the same magnitude as for the barium cadmium bromide, and persist, with increase in dilution, to almost exactly the same extent. The differences for the double bromide of sodium and cadmium are very great in the more concentrated solutions, and diminish comparatively slowly with increase in dilution. Indeed, at a dilution of 7,000 liters the difference is still 33 conductivity units. The differences for the double bromide of ammonium and zinc are large in the more concentrated solutions, but not as large, for equal dilution, as for the double bromide of sodium and cadmium. Furthermore, these differences decrease much more rapidly with increase in dilution, entirely disappearing at about 1,000 liters. We did not study the effect upon one another of mixtures of bromides incapable of forming double salts, partly from lack of time, and partly because it is almost certain that the same general result would be obtained as with the chlorides.

From the above results with double bromides we think we are justified in drawing the same conclusion as in the case of the double chlorides; *viz.*, that *all four of the double bromides studied exist, to a considerable extent, in the more concentrated solutions, and are completely broken down by water only at very great dilutions.*

Ostwald[1] has made a sharp distinction between "double salts" and "complex salts." "The name double salt is not to be applied to any compound of two salts, which shows other reactions than its constituents. In all of these cases the constituents have undoubtedly united to form a more complex compound, which yields new ions, and must be regarded as a unit." Potassium platinum chloride is cited as a typical complex compound, since it breaks down with water into 2Na and $PtCl_6$. The double compounds, according to Ostwald, can be easily distinguished, since the lowering of the freezing-point and rise in boiling-point produced by them, are simply the sum of those produced by the constituents. Similarly, the electrical conductivity is the sum of the conductivities of the constituents.

In terms of this distinction, the double chlorides and bromides, which we have studied, cannot be classed as true double salts, since their conductivity is not the sum of the conductivities of their constituents. This obtains for all, in the more concentrated solutions, but, what is of far greater importance in this connection, it obtains, for several of the salts investigated in very dilute solutions. This is true especially of strontium cadmium chloride, of barium cadmium bromide, and of ammonium zinc bromide.

Before we can determine whether these salts are true complex salts, their solutions must be electrolyzed. If they are salts of true complex acids, when they are electrolyzed the more alkaline metal will go to the cathode, and the more acid metal to the anode. Thus, strontium cadmium chloride would break down in water into a strontium cation, and the cadmium would combine with the chlorine, forming the anion, just as the salt, K_2PtCl_6 breaks down into the ions K_2 and $PtCl_6$.

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[1] Ztschr. phys. Chem., 3, 599.

This problem we propose to investigate. We shall subject both the more concentrated and the more dilute solutions of double halides to the action of the current, and thus learn the nature of the ions formed.

We also propose to investigate a number of other classes of double or complex compounds, to see how they are broken down by water. We also hope to be able to subject some of these to the action of solvents other than water, to see how they are broken down by the different solvents.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1899.

Contributions from the Sheffield Laboratory of Yale University.

LXXI.—ON THE REARRANGEMENT OF THE THIONCARBAMIC ESTERS.

BY H. L. WHEELER AND BAYARD BARNES.

In the year 1849 Debus[1] found that when xanthogenamide, sulphourethane, sulphocarbamic ethyl ester or ethyl thioncarbamate[2] is heated, it is decomposed into ethyl mercaptan and cyanuric acid. This is, perhaps, not what would be expected of a compound having the structure $H_2NCS.OC_2H_5$. Its structure is shown, however, by its method of preparation from the xanthogenic esters and ammonia:

$$C_2H_5OCS.\boxed{SC_2H_5 \quad H}NH_2 = C_2H_5OCS.NH_2 + HSC_2H_5.$$

With alkali it is decomposed normally, according to Debus,[3] into alcohol and sulphocyanate. C. Liebermann,[4] commenting on this behavior in 1881, states: "Es ist nicht unmöglich, dass man diese Reaction durch eine Umlagerung vielleicht in das von Salomon[5] entdeckte carbonylsulfäthylamin

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[1] Ann. Chem. (Liebig), 72, 18.

[2] In naming these substances the writer has employed the Geneva nomenclature *thion* and *thiol.* By this means the position of the sulphur can best be indicated, *thion* being used for compounds containing the group —CS.OR, and *thiol* for those containing the group —CO.SR.

[3] Ann. Chem. (Liebig), 75, 149.

[4] *Ibid.*, 207, 165.

[5] J. prakt. Chem. [2], 7, 256.

[ethyl thiolcarbamate $H_2NCO.SC_2H_5$] erklären muss, wofür auch der Umstand spricht, das die einmal begonnene Reaction von selbst fortschreitet."

Liebermann, however, did not test this explanation or assumption.

It seemed to the writer that if the thioncarbamic esters are capable of rearrangement into the isomeric thiol derivatives this reaction would be aided by alkyl iodides. The iodides would unite with the esters forming, at least, an intermediate addition-product—somewhat analogous to the sulphonium compounds—which would then give up alkyl iodide in another manner.

This seemed probable, as Jeanjean[1] found that dithiocarbamic ethyl ester gives a crystalline compound with ethyl iodide, $H_2NCS.SC_2H_5 + C_2H_5I$, while the work of Claus,[2] Bernthsen,[3] Wallach,[4] and others has shown that the thioamides in general form similar addition-products with alkyl halides.

We therefore heated 10 grams of ethyl thioncarbamate with 5 grams of ethyl iodide for a number of hours in a sealed tube, at 92°–96°. On cooling and opening the tube ethyl mercaptan and a compound having the properties of cyanuric acid were obtained. Under these conditions the reaction had proceeded as Debus found when the amide was submitted to distillation. Evidently this treatment was too energetic.

We then tried the action of ethyl iodide at ordinary temperature, when it was found that the rearrangement took place readily.

With methyl iodide the rearrangement is most striking. When methyl thioncarbamate (methyl xanthogenamide), melting at 43°, is mixed with a molecular proportion of methyl iodide, it dissolves, the temperature of the solution sinks, and then in a few minutes becomes warm enough to boil off the methyl iodide, and the whole solidifies to a shining mass of flattened prisms or plates. The material, after this treatment, melts at 105°–107°, and is, in fact, methyl thiolcarbamate, the carbonylsulfmethylamine of Blankenhorn.[5] The methyl group has been transferred from the oxygen to the sulphur, and the thion compound has been transformed into a thiol :

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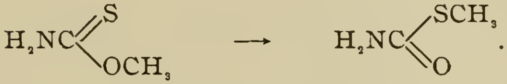
[1] Jahresb., (1866), 501.

[2] Ber. d. chem. Ges., 8, 41.

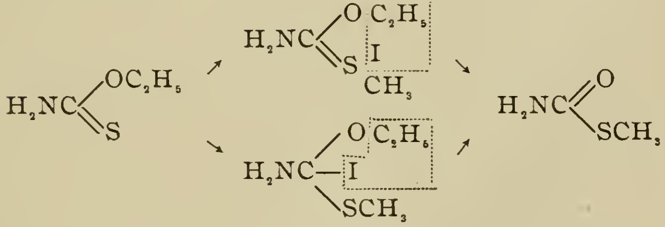
[3] Ann. Chem. (Liebig), **192**, 56.

[4] Ber. d. chem. Ges., **11**, 1594.

[5] J. prakt. Chem., **16**, 379.



This interesting rearrangement is undoubtedly the result of a series of reactions, the alkyl iodide separating into its constituents, alkyl and iodine, the constituents being added to the sulphur, and then separating alkyl from the oxygen along with iodine from the sulphur. This, perhaps, is best shown by the behavior of ethyl thioncarbamate (ethyl xanthogen amide) with methyl iodide, the action taking place with the same ease as with the methyl compound. This may be represented in either of the following two ways :



That is, either the alkyl iodide forms a tetravalent sulphur addition-product or it is added to the double union between sulphur and carbon. At any rate, from ethyl thioncarbamate and methyl iodide, methyl thiolcarbamate and ethyl iodide are obtained.

We have prepared a series of thioncarbamic esters and find that they all undergo this change easily with alkyl iodides. This rearrangement, moreover, is not confined to the action of iodides. Ethyl bromide, and even ethyl chloride, converts ethyl thioncarbamate into ethyl thiolcarbamate.

It might be expected now that ethyl thioncarbamate with ethylene bromide would give the compound

$$H_2NCO.SCH_2.CH_2.Br.$$

This, however, is not the case. As commonly observed with ethylene bromide, both halogens react at once, and the ethylene ester of thiolcarbamic acid results,

$$H_2NCOSCH_2CH_2SCONH_2,$$

along with ethyl thiolcarbamate, the latter resulting from the action of ethyl bromide which is evolved in the reaction.

George Pinkus,[1] in his work on the action of trimethylene chlorobromide on thioamides, obtained in the case of xanthogenamide, a product to which he assigns the empirical formula

$$C_4H_8NOS\frac{Br + Cl}{2}.$$

He states that in the reaction ethyl bromide was evolved and the product melting from 102°–103° gave with potassium hydrate an offensive odor. It is now evident that in this experiment Pinkus had effected a rearrangement of the xanthogenamide without recognizing it, and that his product corresponds to a mixture of equal parts ω-chlor- and ω-brompropyl thiolcarbamates.

We have found that ethyl thioncarbamate reacts readily with chloracetic acid and other halogen compounds. These reactions will be described in a later paper. At present we have not examined the substituted thioncarbamic esters $RNHCSOR'$ and $RNR''CSOR'$, but we intend to do this later.

The above rearrangements, taking place as they do at ordinary temperatures, alter our views in regard to the structure of certain salts of thio- or sulphocarbamic acids. Neither thioncarbamic acid, $H_2NCS.OH$, or thiolcarbamic acid, H_2NCOSH, is known, and according to Beilstein[2] only salts of thiolcarbamic acid have been obtained.

The formation of the ammonium salt, when carbon oxysulphide and ammonia combine,[3] is represented as follows :

$$COS + 2NH_3 = H_2NCO.SNH_4.$$

This thiol structure was established by the work of Fleischer,[4] who found that the salt gives with ethyl bromide at 100°, ethyl thiolcarbamate. Fleischer therefore concluded that this result settled his controversy with Claus,[5] who considered the compound a thion derivative. Previously, Kretzschmar[1] assigned the thiol structure to this salt, chiefly because it gives urea and hydrogen sulphide when heated. Schmidt[2] came to the same conclusion.

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[1] Ber. d. chem. Ges., **26**, 1077.

[2] Handbuch d. org. Chem. [3], **1**, 1258.

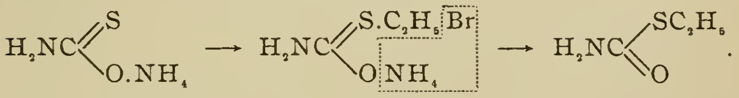
[3] Berthelot : Jahresb., (1868), 160.

[4] Ber. d. chem. Ges., **9**, 991.

[5] *Ibid.*, **9**, 723.

Since now the action of ethyl bromide cannot be used to distinguish between a thiol or thion structure in this class of substances, it seems to the writer that the view of Claus is the best; *i. e.* the ease with which this salt is desulphurized points to the formula $H_2NCSONH_4$. This view is confirmed by the fact that $H_2NCS.OC_2H_5$ is readily desulphurized by silver nitrate while $H_2NCOSC_7H_7$ gives a stable silver salt.

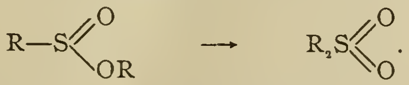
The action of ethyl bromide on this salt is therefore to be represented in precisely the same manner as shown above in the case of the thioncarbamic esters :



The questions now arise : Is this reaction a general one for thion compounds ? Will compounds of the structure ROCS.OR give ROCO.SR, and ROCS.SR be transformed into RSCO.SR? Do the salts of the thioncarbonic acids react tautomerically with alkyl halides ?

With the exception of the above series and the alkyl sulphur derivatives of carbonic acid little is known of the thion compounds containing the grouping $—CS.OC_2H_5$. One salt of thionethylcarbonic acid has been described. Klason[3] states that carbon sulphochloride, $CSCl_2$, and sodium ethylate give $C_2H_5OCSONa$. With this exception it is noteworthy that all the salts of thio- and dithiocarbonic acids hitherto described have the thiol structure assigned to them.

This work also suggests that under suitable conditions a rearrangement may perhaps be expected in the case of tetravalent sulphur compounds ; for example, a shifting of alkyl from oxygen to sulphur may be expected in the case of the esters of the sulphinic acids thus giving sulphones :



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[1] J. prakt. Chem., **7**, 475.

[2] Ber. d. chem. Ges., **10**, 191.

[3] *Ibid.*, **20**, 2384.

The alkyl sulphites may be transformed into alkyl sulphonic esters, etc.,

$$C_2H_5O—SO—OC_2H_5 \longrightarrow C_2H_5SO_2OC_2H_5.$$

Preliminary experiments by Mr. T. B. Johnson with benzenesulphinic ethyl ester and by Mr. R. J. Donnelly with ethyl dithiocarbonate, $C_2H_5OCSSC_2H_5$, show that these compounds are not transformed under the same conditions as the thioncarbamic esters, there being little, if any, tendency of the former, less positive, molecules to undergo change with ethyl iodide.[1]

In the case of the alkali and ammonia salts of thioncarbonic acid the molecule is even more positive than in the case of the thioncarbonic esters; therefore it appears that these compounds should react tautomerically.

We wish to reserve for this laboratory the examination of these questions and the study of the rearrangement of thion derivatives with organic halogen compounds in general, and work along these lines is now in progress here.

EXPERIMENTAL PART.

The thioncarbamic esters were prepared in the usual manner by the action of ammonia on the dithiocarbonic esters, and the latter were prepared by means of ethyl bromide from the potassium xanthogenates.

Methyl Thiolcarbamate from Methyl Thioncarbamate.—One gram of the latter was mixed with 1.5 grams of methyl iodide. On dissolving the solution became cool, then warm, and the product separated in a solid mass of crystals melting at 105°–107°. On crystallizing from water it melted at 107°–108°.

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[1] It seems that basicity plays an important part in these addition reactions. It is probably due to the basicity of the molecules that the salts of the sulphinic acids give sulphones, and that the salts of sulphurous acid give the unsymmetrical derivatives with alkyl halides. Owing to the acid character of the molecules it appears improbable that the nitrites will be changed to the nitroparaffins by alkyl iodides. In the case of the more positive salts of nitrous acid, which act tautomerically, the behavior is precisely what would be expected of an addition-reaction. The higher alkyl iodides, which in general have less tendency to take part in addition-reactions, owing perhaps to stereochemical interference, give chiefly nitrites with these salts, while in the case of the lower halides the nitroparaffins result. In this connection the inertness of β-ethoxycrotonic ethyl ester may be mentioned. This compound can be heated with ethyl iodide for hours at 170°–180° without being converted into ethyl acetoacetic ester, and it can be boiled with benzoyl chloride and recovered unaltered.

Blankenhorn[1] obtained this compound from potassium sulphocyanide, methyl alcohol, and hydrochloric acid, but probably not in a pure condition, since he states that the melting-point lies between 95° and 98°. In all other respects our compound agrees with Blankenhorn's description. In 20 per cent alcoholic solution it gave a yellowish-white, curdy precipitate with silver nitrate. Platinum chloride gave an orange-yellow. mercuric chloride a white, and cupric sulphate a dirty white precipitate. These precipitates did not alter on standing.

Methyl thiolcarbamate is easily soluble in ether and in alcohol, but less readily in water, from which it separates in large, shining, colorless plates that have a talc-like consistency. It is somewhat volatile with steam. Warmed with aniline it evolves methyl mercaptan and ammonia and diphenylurea remains. This carbamate is identical in every respect with the following:

Methyl Thiolcarbamate from Ethyl Thioncarbamate.—The ethyl thioncarbamate used in this and other experiments melted at from 40°–41° and not at 38°, as stated by Salomon.[2] It was purified by dissolving it in ether and precipitating with petroleum ether, when it was obtained in beautiful, square, thick tables.

When 5.5 grams of this material were dissolved in 10 grams of methyl iodide the solution became cold, but on standing a few minutes heat was evolved, and a mass of plates separated. On crystallizing these from water they melted at 107°–108°. A nitrogen determination gave the following result:

	Calculated for		
	$H_2NCO.SCH_3$.	$H_2NCOSC_2H_5$.	Found.
N	15.38	13.33	15.84

It was found that the melting-points of methyl and ethyl thiolcarbamates are identical; they melted side by side at the same temperature in the same apparatus. In order, therefore, to confirm our analytical result and prove that methyl and not ethyl thiolcarbamate results in this reaction, Mr. W. M. Saunders performed the following experiment to determine whether our product with aniline gives methyl mercaptan (a gas) or ethyl mercaptan (a liquid boiling at 36°), and also to identify the products of the reaction: Two grams of the product obtained by acting on ethyl thioncarbamate with methyl iodide were heated with about 2 molecules of aniline to 160° in an oil-bath, when over 350 cc. of gas was obtained which was collected over water. Ammonia and the odor of mercaptan were noticed. The gas passed into a solution of mercuric cyanide gave a finely divided white precipitate, which, purified by means of alcohol, in which it is very difficultly soluble, melted with decomposition at 170°–175°. The residue left on heating was crystallized from alcohol when diphenylurea was obtained melting at 234°–236°. There is, therefore, no doubt that methyl thiol carbamate is formed in the above reaction, and the action with aniline proceeds as follows:

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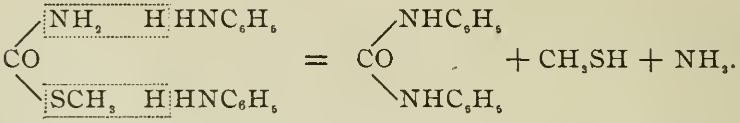
[1] J. prakt. Chem. [2], **16**, 375.

[2] *Ibid.* [2], 8, 115.



$$CO\begin{array}{l}\diagup \boxed{NH_2 \quad H}HNC_6H_5 \\ \diagdown \boxed{SCH_3 \quad H}HNC_6H_5\end{array} = CO\begin{array}{l}\diagup NHC_6H_5 \\ \diagdown NHC_6H_5\end{array} + CH_3SH + NH_3.$$

Ethyl Thiolcarbamate from Ethyl Thioncarbamate.—When a portion of ethyl thioncarbamate (xanthogenamide) was dissolved in ethyl iodide, and the solution allowed to stand, a mass of silver-white plates remained after spontaneous evaporation of the iodide. These melted at 107°–108°. Another portion was allowed to stand only an hour when the material melted below 60°, the rearrangement then, not being complete, the solution was warmed on the water-bath, when it soon solidified. This rearrangement, therefore, takes place with greater difficulty than in the case of the methyl carbamate. The material in this instance, melting at 107°–108° and needing no purification, was simply pressed on paper and dried in the air. A nitrogen determination gave the following:

	Calculated for $H_2NCO.SC_2H_5$.	Found.
N	13.33	13.02

This product gave the reactions for "carboxylsulfäthylamin" as described by Konrad and Salomon.[1] Although, as stated, the melting-point of this compound is identical with that of the methyl derivative, a mixture of the two was found to melt below 89°.

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[1] J. prakt. Chem., 10, 35.

In another experiment ethyl thioncarbamate (5 grams) and ethyl bromide (6 grams) were heated for an hour on the water-bath, when it was found that a rearrangement had taken place, the product being identical with the above.

Isopropyl Thiolcarbamate from Isoamyl Thioncarbamate.—Ten grams of the latter were heated with 12 grams of isopropyl iodide on the steam-bath for two days. On cooling, a mass of crystals was obtained. These were washed with warm petroleum ether and crystallized twice from water when the material was obtained in colorless rectangular plates melting at about 125°. A nitrogen determination gave :

	Calculated for $H_2NCOSC_3H_7$.	Found.
N	11.76	11.84

The behavior of this material with silver nitrate, mercuric chloride, copper sulphate, and platinum chloride is identical with that of isobutyl thiolcarbamate and the other members of this series.

Isobutylthion carbamate was obtained by Mylius[1] from "isobutyldioxysulfocarbonat" and alcoholic ammonia. He states that it forms yellowish-white tables (from alcohol) melting at 36°. Blankenhorn[2] obtained this mixed with the thiol compound by treating potassium sulphocyanide in isobutyl alcohol with hydrochloric acid. He describes his product as a yellow oil crystallizing at 6° and melting at 10°. Our compound prepared from $C_5H_{11}O.CS.SC_2H_5$ and alcoholic ammonia readily solidified, and on crystallizing once from ether and then from water, melted at 51°–53°. It forms a snow-white mass of plates, and a nitrogen determination gave the following :

	Calculated for $H_2NCS.OC_4H_9$.	Found.
N	10.52	10.40

Isobutyl thioncarbamate in dilute alcoholic solution gives with silver nitrate a white precipitate which soon turns black (difference from thiolisobutylcarbamate). Mercuric chloride gives a white precipitate which can be boiled with water without change of color. Copper sulphate gives a white precipitate which, when warmed, changes to black. Platinum chloride gives a yellow precipitate which, when warmed, decomposes.

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[1] Ber. d. chem. Ges., **5**, 976.

[2] J. prakt. Chem. [2], **16**, 380.

Isobutyl Thiolcarbamate from Isobutyl Thioncarbamate.—Five grams of the above material, melting at 51°–53°, were heated with 1 gram of isobutyl iodide, on the water-bath, for two hours, and on taking out a portion it was found to melt unaltered at 51°–53°. It was then heated in an oil-bath to 120° for several hours. On cooling, and crystallizing the material from water, it was then found to melt at 102°–103°. It thus separates in magnificent snow-white plates of extreme thinness. A nitrogen determination gave:

	Calculated for $H_2NCOSC_4H_9$.	Found.
N	10.52	10.45

Isobutyl thiolcarbamate closely resembles the other members of the thiol series. It is readily soluble in the ordinary solvents, except cold water, and it is volatilized with steam. Silver nitrate added to its dilute alcoholic solution produces a white precipitate which does not alter on standing. With mercuric chloride it behaves like the thion compound. With copper sulphate no precipitate is obtained in the cold, but on warming a white precipitate separates. Platinum chloride gives no precipitate in dilute solution.

Isoamyl Thiolcarbamate from Isoamyl Thioncarbamate.—Isoamyl thioncarbamate, as prepared in 1853 by M. W. Johnson[1] from "binoxysulphocarbonate of amyl" and ammonia was an oil. Our material also was obtained as an oil which refused to solidify on cooling. When heated (10 grams) with isoamyl iodide (5 grams) at 120°–130° for several hours, it was transformed slowly and less completely than the lower members of this series. The product, crystallized from hot water, formed extremely large, silver-white plates resembling thin slices of mica. It melted at 112°–113°, while Schöne[2] says that isoamyl thiolcarbamate forms plates melting at 107°, when prepared from the chloride $C_5H_{11}SCOCl$ and ammonia. A nitrogen determination gave:

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[1] Quart. J. Chem. Soc., **5**, 142.

[2] J. prakt. Chem. [2], **32**, 247.

	Calculated for $H_2NCO.SC_5H_{11}$.	Found.
N	9.52	9.16

Isoamyl thiolcarbamate does not differ in properties from the other members of the series. With silver nitrate, mercuric chloride, copper sulphate, etc., it behaves precisely like isobutyl thiolcarbamate.

Ethyl Thioncarbamate and Ethylene Bromide.—When 10 grams of the former and 37 grams of the latter were mixed, and heated on the steam-bath for three hours, ethyl bromide was evolved and, on cooling, a crystalline mass was deposited. It was purified by boiling with alcohol and water, which extracts ethyl carbamate, and was thus obtained as a crystalline powder which was quite difficultly soluble in the ordinary solvents. It was free from bromine, and a nitrogen determination gave the following :

	Calculated for $C_4H_8S_2N_2O_2$.	Found.
N	15.55	14.99

Ethyl Benzenesulphinate, $C_6H_5SO.OC_2H_5$, *with Methyl and Ethyl Iodides.*—The following negative experiments were performed by Mr. T. B. Johnson, to whom we wish to express our thanks. 4 grams of the ethyl ester were heated with 3.6 grams of ethyl iodide at 100°–110° for one hour, when no apparent reaction took place. On further heating, the material darkened but it deposited no crystals when placed in a freezing mixture. Heated further for four hours at 130°–140° considerable decomposition took place. The material, extracted with ether, washed with sodium hydroxide, dried, and evaporated, gave no solid material.

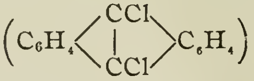
Ten grams of the ester were heated with 8.3 grams methyl iodide for one hour at 110°–120°, then again at 145°–155°. On opening the tube there was much pressure and a thick black oil resulted. This was extracted with ether and washed with sodium hydroxide. On evaporation, 2.5 grams of black oil was obtained which refused to solidify and when heated began to boil at 100° ; then the temperature rose to 250°, when the remaining material charred. Ethyl phenyl sulphone boils unaltered above 300°, and melts at 42°. Methyl phenylsulphone melts at 88°.

NEW HAVEN, CONN., May, 1899.

Contributions from the Chemical Laboratory of Cornell University.

DIMETHYLDIANTHRACENE: A POLYMERIC MODIFICATION OF β-METHYLANTHRACENE.

By W. R. Orndorff and H. A. Megraw.

In a previous paper[1] by one of us it was shown that anthracene, when suspended in benzene and exposed to the sunlight, was rapidly polymerized to a compound having the same percentage composition as the original product but twice the molecular weight. For this product we suggested the name dianthracene instead of paranthracene, as more exact and more scientific. Attempts to prepare derivatives of dianthracene by treating this substance directly with various reagents were unsuccessful, as the polymer was changed into the simple substance, anthracene, under these conditions, and derivatives of anthracene itself were always obtained. We then tried to prepare substitution-products of dianthracene by subjecting derivatives of anthracene to the action of the sunlight. In this way we succeeded in making dihydroxydianthracene (dianthranol)[2] from anthranol (γ-hydroxyanthracene). We further found that when both of the γ-hydrogen atoms were replaced by chlorine, the substance, dichloranthracene  $\left(C_6H_4\left\langle\begin{matrix}CCl\\ |\\ CCl\end{matrix}\right\rangle C_6H_4\right)$, was no longer polymerized by the action of the sunlight.

It seemed to us highly probable that the α- and β-derivatives of anthracene would polymerize in the same way that anthracene itself does since both these derivatives contain the same meso groups, the change in which we found to be the cause of the polymerization in the case of that hydrocarbon. In this way it seemed possible to prepare substitution-products of dianthracene.

The first substance studied was β-methylanthracene, which we found underwent polymerization in the sunlight just as readily as anthracene, forming a compound with the same percentage composition but twice the molecular weight of methylanthracene and which we have, therefore, named dimethyldianthracene.

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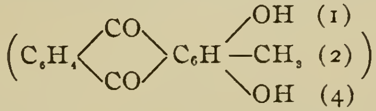
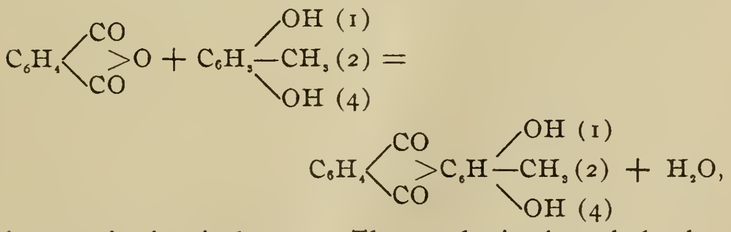
[1] This Journal, 17, 658.

[2] *Ibid.*, 18, 453.

β-Methylanthracene, $C_{15}H_{12}$, was first obtained by Weiler[1] and O. Fischer,[2] in 1874, by conducting the vapors of dimethylphenylmethane and dimethylphenylethane through a red-hot tube. G. Schultz[3] then found the hydrocarbon among the products formed by heating the oil of turpentine to a comparatively high temperature. Schultz suggested that the compound would be found in coal-tar, and later, working together with Japp,[4] he succeeded in isolating this hydrocarbon from that complex mixture. Wackendorff and Zincke[5] then showed that it is formed in the decomposition of high boiling aniline oils. Nietzke[6] made the substance by heating methyl quinizarin,  $\left(C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}C_6H\begin{matrix}\diagup OH\ (1)\\ -CH_3\ (2)\\ \diagdown OH\ (4)\end{matrix}\right)$, with zinc dust, thus showing that it was a β-compound. Later this same β-methylanthracene was also shown to result from the distillation of several plant substances, such as emodin, chrysophanic acid,[7] abietinic acid,[8] and crysarobin[9] with zinc dust. The constitution of this hydrocarbon is determined from its formation[10] from methyl quinizarin by heating this substance with zinc dust. As the methyl quinizarin results from heating phthalic anhydride and hydrotoluquinone together in the presence of sulphuric acid in accordance with this equation :



$$C_6H_4\begin{matrix}\diagup CO\\ \\ \diagdown CO\end{matrix}\!\!>O + C_6H_3\begin{matrix}\diagup OH\ (1)\\ -CH_3\ (2)\\ \diagdown OH\ (4)\end{matrix} = C_6H_4\begin{matrix}\diagup CO\\ \\ \diagdown CO\end{matrix}\!\!>C_6H\begin{matrix}\diagup OH\ (1)\\ -CH_3\ (2)\\ \diagdown OH\ (4)\end{matrix} + H_2O,$$

its constitution is known. The synthesis of methylanthracene from *p*-xylyl phenyl ketone, $C_6H_5COC_6H_3(CH_3)_2$, accomplished by Elbs and Larsen[1] also leads to the same conclusion, that the methylanthracene is the *β*-compound and has the following constitution :

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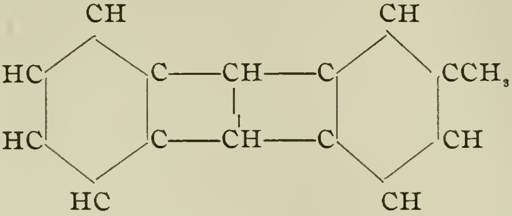
[1] Ber. d. chem. Ges., **7**, 1185.
[2] *Ibid.*, **7**, 1195.
[3] *Ibid.*, **10**, 117.
[4] *Ibid.*, **10**, 1049.
[5] *Ibid.*, **10**, 1485.
[6] *Ibid.*, **10**, 2013
[7] Liebermann : Ann. Chem. (Liebig), **183**, 163 ; **163**, 169.
[8] Ciamician : Ber. d. chem. Ges., **11**, 273.
[9] Liebermann and Seidler : Ann. Chem. (Liebig), **212**, 34 ; Ber. d. chem. Ges., **11**, 1605.
[10] Ber. d. chem. Ges., **10**, 2013.



This *β*-methylanthracene is described as crystallizing in yellow plates (which, however, are perfectly white when pure and show a bluish fluorescence), melting at 199°–200° C. and boiling above 360° C. It is but slightly soluble in alcohol, ether, and glacial acetic acid, though readily soluble in carbon bisulphide and benzene. With picric acid it combines to form a characteristic compound crystallizing in red needles and resembling the anthracene compound with picric acid very closely. The action of sunlight on *β*-methylanthracene has, so far as we are aware, never been investigated.

The product with which we started was purchased from Schuchardt and presumably was obtained from coal-tar. It had the melting-point and all the other properties characteristic of *β*-methylanthracene. When suspended in benzene in white glass bottles and exposed to the action of the sunlight during the summer of 1897 it was rapidly polymerized, forming a white crystalline substance which, when recrystallized several times from toluene, was found to melt with slight decomposition at 228°–230° C. The melting-point of this slightly decomposed product was 200° C. (the melting-point of *β*-methyl anthracene). From this it seemed highly probable that *β*-methylanthracene suffers a similar change in the sunlight to that which anthracene itself undergoes, and moreover that the polymeric product when heated to its melting-point is reconverted into the simple substance from which it was formed exactly as in the case of dianthracene. A considerable quantity of the polymeric product was now made by the method used in the preparation of dianthracene. It was then purified by boiling with alcohol, acetic acid, and benzene, to remove any substances soluble in these liquids, and by recrystallizing the product, thus purified, four times from toluene. The products of the different crystallizations were checked by combustion analyses. Many analyses were made but a pure product was obtained only after four recrystallizations from toluene. The following are the results of the last four analyses made with this product:

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[1] Ber. d. chem. Ges., **17**, 2849. See also in this connection Hammerschlag : *Ibid.*, **11**, 82.

I. 0.2145 gram substance gave 0.7387 gram CO_2 and 0.1183 gram H_2O.

II. 0.1610 gram substance gave 0.5536 gram CO_2, and 0.0909 gram H_2O.

III. 0.2156 gram substance gave 0.7398 gram CO_2, and 0.1184 gram H_2O.

IV. 0.1611 gram substance gave 0.5537 gram CO_2, and 0.0908 gram H_2O.

	Calculated for		Found.			
	$C_{15}H_{12}$.	$C_{14}H_{10}$.	I.	II.	III.	IV.
C	93.75	94.38	93.92	93.78	93.58	93.74
H	6.25	5.62	6.13	6.27	6.10	6.26
	100.00	100.00	100.05	100.05	99.68	100.00

These results show that the product formed by the action of sunlight on solutions of β-methylanthracene in benzene has the same percentage composition as β-methylanthracene itself.

Molecular weight determinations were then made with the pure product, using the boiling-point method and toluene and pyridine as solvents. In making these determinations we used the boiling-point apparatus devised by Orndorff and Cameron,[1] and followed closely the directions given by them. The following are the results obtained:

Molecular Weight Determinations.

β-Methylanthracene, $C_{15}H_{12} = 192$; dimethyldianthracene, $C_{30}H_{24} = 384$. Solvent: toluene, boiling-point 109°.7 at 741.7 mm. Molecular rise for 100 grams 35.1.°

[1] This JOURNAL, 17, 517.

Solvent. Grams.	Substance. Grams.	Observed rise.	Molecular weight found.
83.88	0.5238	0.054°	404
	0.9244	0.089°	433
	2.0109	0.189°	445
	2.3805	0.229°	434
	2.8347	0.271°	437
	Average of five determinations		431

Barometer constant.
Molecular weight at infinite dilution 387

A second series in toluene gave the following results :

Solvent. Grams.	Substance. Grams.	Observed rise.	Molecular weight found.
99.08	0.4340	0.042°	366
	0.9521	0.083°	406
	1.4011	0.123°	403
	1.8997	0.167°	359
	2.5663	0.216°	421
	Average of five determinations		391

Barometer constant.
Molecular weight at infinite dilution 390

With pyridine the following results were obtained :

Solvent : pyridine. Boiling-point 114.2° at 741.7 mm. Molecular rise for 100 grams, 26.9°.

Solvent. Grams.	Substance. Grams.	Observed rise.	Molecular weight found.
117.1	0.3242	0.020°	371
	0.6511	0.033°	452
	0.9749	0.051°	438
	1.2941	0.070°	424
	1.5051	0.081°	425
	Average of five determinations		422

These results show that the substance has the molecular weight 384, or twice that of β-methylanthracene, and that it is hence dimethyldianthracene.

The pure product is a white crystalline substance which melts with slight decomposition at 228°–230° (uncorr.) or even lower when the heating is prolonged at the lower temperature. The slightly decomposed product resulting was found to melt at 200° C. (the melting-point of β-methylanthracene), and to be β-methylanthracene, as it gave with picric acid a compound crystallizing in dark-red needles and melting at 199° C., identical with the β-methylanthracene picric acid compound. The product is therefore a polymer of β-methylanthracene and is changed into this substance when heated to its melting-point. This transformation can be accomplished at a much lower temperature than the melting-point of the polymeric product (228°–230° C.), in boiling liquids in which it is soluble, for example, in anisol, which boils at 155° C., and to some extent in boiling metaxylene (139° C.).

Pure dimethyl dianthracene shows none of the bluish fluorescence so characteristic of pure anthracene and β-methylanthracene. With picric acid it forms no compound. It was not found possible to obtain either β-methylanthracene or dimethyldianthracene in the form of crystals large enough to measure and determine the system ; but from its optical properties dimethyldianthracene is either orthorhombic or monoclinic, more probably orthorhombic, while β-methylanthracene is probably monoclinic. Dimethyldianthracene is almost insoluble in all solvents in the cold, and even at the boiling temperature it is but slightly soluble in alcohol, ether, acetone, acetic ether, carbon disulphide, and chloroform. In benzene, toluene, and xylene, at their respective boiling-points, it is somewhat more soluble, the solubility increasing with the boiling-point of the solvent. There are several plant substances, such as emodin, chrysophanic acid, and chrysarobin, which, when distilled with zinc dust, give β-methylanthracene. As these substances are formed in the direct sunlight and undoubtedly contain a residue of β-methylanthracene it is quite possible that they may be derivatives of dimethyldianthracene. Further work will be undertaken in this laboratory to see if derivatives of dimethyldianthracene exists in nature and also to prepare further derivatives of dianthracene.

CORNELL UNIVERSITY, May, 1899.

THE ACTION OF CHROMIC ACID ON HYDROGEN.

BY CHAS. L. REESE.

In 1872 E. Ludwig[1] published an article on the action of chromic acid on carbon monoxide, hydrogen, marsh-gas, and ethylene, in which he described experiments from which he drew the conclusion that hydrogen is oxidized by a saturated solution of chromic acid under ordinary conditions.

He saturated gypsum balls with a saturated water solution of pure chromic acid and placed these in an atmosphere of hydrogen in tubes over mercury. He gives the figures from one experiment in which 35.8 cc. of gas were completely absorbed in eighty-six hours at 17°–18° C. This article is quoted in a number of reference works as authority for the statement that hydrogen is oxidized by chromic acid.

I repeated Ludwig's experiment a number of times, using not only gypsum but also porous burnt clay balls, and in each case confirmed his results, with this exception, that in no case was all of the hydrogen absorbed, and in the case of the clay balls a much smaller volume was absorbed than in the case of gypsum, some of them having been allowed to stand fifteen to twenty days without showing any change of volume after the first few days.

The chromic acid in the balls was shown to be partly reduced, by the greenish-brown solution obtained from them in water after the reaction. This reduction of chromic acid by hydrogen, however, took place in the presence of a porous material which is known in many cases to aid reaction, and I found in later experiments that the reaction would also take place at the temperature of the room by agitating pure chromic acid solution with hydrogen in sealed tubes containing platinum asbestos, although it would not act in the presence of platinum foil.

When sulphuric acid was added to the chromic acid solution in presence of platinum asbestos the absorption of hydrogen took place much more rapidly, as would be expected.

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[1] Ann. Chem. (Liebig), **162**, 47.

To determine whether hydrogen was oxidized at all by a saturated solution of pure chromic acid, I at first used graduated gas-measuring tubes with stop-cocks at both ends, the tubes being first filled with the solution and the gas introduced, by displacement, from an electric generator, such as described by Magruder,[1] but these proved unsatisfactory, owing to the action of chromic acid on the grease in the stop-cocks, so that glass tubes were substituted, with capillaries drawn on both ends, which could be sealed and opened without loss of gas. They were filled with the solution and, after the introduction, through capillary rubber connections, of a measured volume of hydrogen from a Hempel burette, were then sealed, the height of the liquid on the tube, under atmospheric condition, being first marked.

A number of these tubes were agitated for from five to fifteen days, by fastening them, by means of clamps which held them at right angles to a revolving shaft which was caused to turn at a rate sufficient to throw the liquid from one end of the tube to the other twice on every revolution.

Pure chromic acid, free from sulphuric and nitric acids was used in some cases and in others concentrated sulphuric acid was added in quantities equal to 1, 2, 5 to 15 per cent by volume; but in no case was the volume of hydrogen found to be changed on opening the tubes, and on analysis the gas was invariably found to be pure hydrogen. It will thus be seen that pure hydrogen is not acted upon by either pure chromic acid solution or one containing sulphuric acid, under ordinary conditions. I next determined to see if the action would not take place at higher temperatures, and for this purpose used tubes similar to those already described except that the chromic acid was introduced into a small bulb containing from 1 to 2 cc. and placed in the tube before the second capillary was drawn out on it. These tubes were then filled with redistilled water and the water displaced by hydrogen, which was measured as before.

The tubes, after the bulbs in them were broken, were at first heated in a Carius furnace to temperatures ranging from

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[1] This Journal, **14**, 810.

150°–190° C. for from three to five hours, and in every case on opening and analyzing the gas some of the hydrogen was found to have disappeared and more oxygen than enough to make up the difference was found to be present. It was also found that by heating tubes containing air in the place of hydrogen, oxygen was evolved, thus showing that the evolution of oxygen was simply due to the decomposition of the chromic acid in water rather than to the influence of the hydrogen. Having found that hydrogen is oxidized by chromic acid at the above temperatures, I determined to find out, if possible, at what temperature the reaction begins and at what temperature a saturated solution of chromic acid begins to give up oxygen, and whether these two points are identical; that is, whether hydrogen is not acted upon by chromic acid till the latter begins to decompose by heat.

The Carius furnace being unsuitable for constant temperatures I devised another arrangement, which proved very satisfactory. I had cylinders made of 2-inch wrought-iron pipe with a plug forged into one end and a threaded cap fitted on the other, which was rendered vapor-tight by suitable washers, and had holes bored through for thermometer and condensing tube. These cylinders were placed in an inclined position with enough liquid in them of the proper boiling-point to insure their being filled with the vapor when boiled. The tubes were placed in the cylinders and kept separated from the sides by wire or glass triangular supports. The cylinders were covered with sufficient asbestos to prevent radiation and protected from air draughts. With these cylinders it was possible to maintain a constant temperature, just as is done with the Victor Meyèr constant temperature bath.

Tubes containing saturated solutions of chromic acid and hydrogen were heated to temperatures ranging from 35°–156° C., the time of heating ranging from five hours for the highest temperature to five hundred hours for the lowest. It will be seen from the accompanying table (I) that there is no evo-

Table I.

	Temperature.	Time in hours.	Hydrogen used. cc.	Hydrogen absorbed. cc.	Oxygen evolved. cc.
1	156°	5	40.6	1.8	7.4
2	"	7	36.0	3.8	19.4
3	138°	7	36.4	3.6	11.8
4	"	6.5	32.7	3.0	6.2
5	135°	8.5	32.2	3.7	5.2
6	111°	5.5	37.4	0.6	0.6
7	"	10	39.6	1.0	1.0
8	100°	16	39.4	0.94	0.6
9	"	25	29.8	9.5	1.2
10	"	60	23.4	22.9	0.6
11	"	116	35.8	25.5	3.7
12	78°	13.5	41.4	0.0	0.0
13	"	25	31.8	0.7	0.0
14	"	25	31.6	0.0	0.0
15	"	32	41.2	2.0	1.7
16	"	60	30.9	5.5	0.5
17	"	90	30.8	2.0	0.8
18	"	120	34.7	7.4	0.7
19	61°	126	39.9	6.5	0.0
20	50°	192	32.1	0.7	0.0
21	"	288	31.0	0.5	0.0
22	40°	260	42.0	0.0	0.0
23	"	240	42.3	0.4	0.0
24	35°	360	42.0	0.0	0.0
25	"	500	44.5	0.2	0.0

lution of oxygen at temperatures below 78° and only in one case, at temperatures below 100°, was the quantity of oxygen very considerable even when heated as long as one hundred and twenty hours. The absorption or oxidation of hydrogen was very considerable at temperatures at and above 61° when heated for a sufficient length of time; but at 50° the absorption was very slight for as much as two hundred and eighty-eight hours heating, and at 40° and below there was no appreciable absorption.

From the results of these experiments I think I can safely say that hydrogen is not oxidized by saturated solutions of chromic acid at temperatures below 50° and that the action is extremely slow below 100°.

The oxygen evolved was measured by absorption in sodium pyrogallate in a Hempel apparatus. All the volumes given are reduced to normal conditions.

In the experiments at 35° the tubes were agitated as in the earlier experiments, on a revolving shaft in a constant temperature air-bath.

Table II shows the results of heating a number of tubes containing air in the place of hydrogen, to determine at what temperature a saturated solution of chromic acid would give up oxygen. These experiments show that such a solution decomposes quite rapidly at temperatures above 119°, and very slowly, indeed, at lower temperatures, ceasing altogether at 78°.

Table II.

	Temperature.	Time in hours. cc.	Oxygen evolved. cc.
1	156°	5	19.0
2	119°	4.5	9.7
3	111°	11	0.3
4	100°	15	0.3
5	"	25	1.3
6	"	30	0.6
7	"	60	1.3
8	78°	135	0.0
9	"	129	0.7

As hydrogen is oxidized at temperatures below those at which oxygen is given off by chromic acid, the oxidation of hydrogen does not seem to be dependent upon the decomposition of chromic acid by heat, in fact at higher temperatures a large excess of oxygen was evolved, above the equivalent of the hydrogen oxidized, while some hydrogen still remained.

It is interesting in this connection to note that Berthelot[1] found that hydrogen is not oxidized by nitric acid at 100°, although nitric acid gives up oxygen at this temperature.

Action of Electrolytic Hydrogen.

I next turned my attention to the action of hydrogen produced electrolytically in a solution of chromic acid. For this purpose a normal solution of chromic acid was used because it could be more readily titrated to determine the amount of

[1] Compt. rend., **127**, 27–29.

reduction. The solution was placed in a burette and platinum electrodes were used, the connections passing through glass tubes into which the electrodes were sealed. The hydrogen electrode was placed at the bottom and the other at the top of the liquid so that the hydrogen gas could pass up through the liquid and the oxygen pass out at the top. Any product of reduction being heavy would remain near the bottom, as was found to be the case in certain solutions, and thus escape oxidation. When the amount of reduction was studied the solution was well mixed from time to time. The long narrow tube was used to prevent spattering and loss by evaporation, and the burette form was used so that the solution could be drawn off from time to time, well mixed, and a portion titrated, the rest being returned to the tube for the purpose of continuing the experiment. The current used was from two storage battery cells so that there was an abundant evolution of hydrogen.

Perfectly pure chromic acid free from any trace of sulphuric acid was not reduced at all after passing the current through for twenty-four hours ; but if it contained the slightest trace of sulphuric acid or a sulphate, reduction took place as was seen in a few minutes from the darkening of the solution and the absorption of the hydrogen ; but there was always a limit reached when no further reduction took place. In the case of a specimen containing a trace of sulphuric acid the reduction was complete after 2.85 per cent had been reduced, although the current was allowed to act for two days after this point had been reached.

Sulphuric acid, potassium sulphate, and chromium sulphate were added to the pure chromic acid solution and in each case reduction took place up to a definite percentage and then stopped. Pure potassium bichromate was not reduced at all, but on addition of sulphuric acid or a sulphate, reduction took place in the same way as with the pure chromic acid to which these substances were added.

The fact that a limit is reached in the electrolytic reduction of chromic acid containing definite quantities of sulphuric acid or a sulphate may lead to a means of determining the quantities of these substances present in a specimen of chromic acid or to a means of determining the relative strength of the two acids. Sufficient data, however, have not yet been obtained for determining this question.

The titrations in these experiments were carried out by reducing the acid with ferrous ammonium sulphate and titrating back with potassium permanganate. The green color of the chromium sulphate does not interfere at all with the end reaction. The method is perfectly reliable as I have compared it with Bunsen's method as well as with the gravimetric method.

The chromic anhydride used in these experiments was obtained from Gehe & Co., of Dresden, and was marked "free from sulphuric acid." One lot of it did not show a trace of sulphuric acid and was extremely pure. I have been able to recrystallize this acid by allowing a saturated water solution of it to stand in a desiccator over calcium chloride. It crystallized in beautiful solid rosettes which appeared almost black by reflected light and a beautiful ruby color by transmitted light. It was suggested that these crystals might be the hitherto unobtained chromic acid, but on analysis they proved to be the anhydride.

JOHNS HOPKINS UNIVERSITY,
May, 1899.

Contributions from the Chemical Laboratory of Purdue University.

ACTION OF SULPHURIC ACID ON NITROHEPTANE.

BY R. A. WORSTALL.

The nitrosulphonic acids constitute a class of compounds practically unknown in the aliphatic series. For while these derivatives are readily obtainable in the aromatic series by nitration of sulphonic acids or by sulphonation of nitro hydrocarbons, no corresponding reactions are known in the case of paraffins.

Victor Meyer[1] has shown that the action of fuming sulphuric acid upon nitroethane gives ethylene disulphonic acid, while concentrated sulphuric acid gives acetic acid as the chief product. In the latter case, however, upon neutralizing the sulphuric acid solution with barium carbonate, he also obtained a barium salt containing nitrogen, but in such minute quantity that he was unable to identify it, although he suspected that it was the salt of a nitrosulphonic acid.[1] Having on hand a small quantity of nitroheptane a study of its reactions with sulphuric acid of different degrees of concentration was undertaken, with the hope of obtaining a nitrosulphonic acid.

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[1] Ann. Chem. (Liebig), 171, 53.

Action of Dilute Sulphuric Acid.

Five grams of nitroheptane (boiling-point 193°–196°) were digested with 50 grams of dilute sulphuric acid (1 part acid to 5 parts water) at about 80° for ten minutes. The solution was cooled, diluted, and extracted with ether. The ether was removed by evaporation. There was a residue (5 grams) with the characteristic odor of the fatty acids. This residue was boiled with water and calcium carbonate, the solution filtered, and silver nitrate added to the filtrate. A white flocculent precipitate was formed. This silver salt was washed, dried, and analyzed.

0.2012 gram gave 0.0923 gram Ag.

	Calculated for $C_7H_{13}O_2Ag$.	Found.
Ag	45.6	45.8

The product of the reaction was therefore heptoic acid, formed as follows:

$$C_6H_{13}CH_2NO_2 + H_2O = C_6H_{13}COOH + NH_3O.$$

Action of Concentrated Sulphuric Acid.

Five grams of nitroheptane were gradually added to an excess of concentrated sulphuric acid (specific gravity 1.84). A reaction took place at once with the evolution of heat. The solution was diluted and extracted twice with ether. The ether was removed from the extract by evaporation and the residue converted into the silver salt in the usual manner. The latter was analyzed.

0.0824 gram gave 0.0380 gram Ag.

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[1] Ann. Chem. (Liebig), 171, 54.

	Calculated for $C_7H_{13}O_2Ag$.	Found.
Ag	45.6	46.1

The sulphuric acid solution which had been twice extracted with ether still retained a yellow color. It was neutralized with barium carbonate, filtered, and the filtrate evaporated to dryness. A small quantity of a yellow salt remained which contained no nitrogen, and was found to be the barium salt of heptoic acid. The action of concentrated sulphuric acid, therefore, is the same as that of the dilute.

Action of Fuming Sulphuric Acid.

Ten grams of nitroheptane were gradually added with constant shaking, to 50 grams of fuming sulphuric acid, kept cold. Some sulphur dioxide was liberated, and upon diluting with water a small quantity of a carbonized residue remained insoluble. Upon allowing the diluted solution to stand, a fatty acid separated as an oil at the top. The solution was repeatedly extracted with ether, the ethereal solution evaporated, and the silver salt of the residue, which amounted to 4 grams, was formed in the usual manner. This silver salt was analyzed.

0.1030 gram gave 0.0465 gram Ag.

	Calculated for $C_7H_{13}O_2Ag$.	Found.
Ag	45.6	45.1

The acid solution left after the extraction with ether was neutralized with barium carbonate, and filtered. The yellow solution thus obtained was evaporated to dryness, leaving as a residue 2 grams of a brown barium salt. Qualitative tests showed the presence of sulphur and of nitrogen. This salt was extracted with boiling 90 per cent alcohol, filtered, and the solution evaporated to a small volume. Upon long standing, small reddish-yellow plates crystallized out. These were removed, dried, and analyzed.

0.1506 gram gave 0.0614 gram $BaSO_4$ (for barium).

0.2175 gram gave 0.1602 gram $BaSO_4$ (for sulphur).

0.1114 gram gave 4.6 cc. nitrogen at 742 mm. and 18°.

	Calculated for $\left(C_7H_{14}<\begin{matrix}SO_3\\NO_2\end{matrix}\right)_2B$	Found.
Ba	23.42	23.97
S	10.94	10.37
N	4.74	4.62

The compound was therefore undoubtedly the barium salt of nitroheptanesulphonic acid. This salt was readily soluble in water and in hot alcohol, differing in the latter respect from barium heptylsulphonate.[1] It crystallized poorly from alcohol in small plates. In all, but 1 gram of the purified salt was obtained from 10 grams of nitroheptane—a yield of but 5 per cent of the theoretical.

Twenty grams of nitroheptane, when sulphonated in the same way, yielded two grams of the barium salt. This was dissolved in water, the barium precipitated with dilute sulphuric acid, the solution filtered, neutralized with lead carbonate, and filtered again. The lead was removed by means of hydrogen sulphide, and the filtrate evaporated to dryness. A small quantity of a thick, brown syrup remained, which could not be purified for analysis.

It is to be regretted that a better yield could not be obtained in order that other reactions might be tried for identification. But it is believed that the method of formation, together with the analysis and properties of the barium salt, afford definite proof of the formation of a nitrosulphonic acid. While there is no proof to that effect, it would seem probable that in the sulphonation of a nitroparaffin, the same law would hold good as in the case of the sulphonation of other substituted paraffins—that is, that the sulphonic acid group attaches itself to the carbon atom adjacent to the one which carries the substituting radical. An attempt was made to prepare a sulphonic acid by acting upon bromnitroheptane, $C_6H_{13}CHBrNO_2$, with sodium sulphite, but without success, as ammonia was evolved each time. The formation of this nitrosulphonic acid is interesting in that it shows another reaction possible in the aliphatic as well as in the aromatic series.

LAFAYETTE, IND., March, 1899.

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[1] This JOURNAL, **20**, 669.

REVIEWS.

CHEMICAL EXPERIMENTS. BY J. F. WOODHULL, Professor of Physical Science, Teachers' College, Columbia College, New York, and M. B. VAN ARSDALE, Instructor in Physical Science in Horace Mann School and Assistant in Teachers' College. New York: Henry Holt & Co. 1899.

On examining this book one is struck with several features which are, unfortunately, not usually found in books of this kind, the principal one being its simplicity. The great amount of material and bewildering mass of details so often found are omitted here; but a few of the elements, and their relation to important processes and substances, are studied, and the broad bearing of the subject developed by suitable questions. An idea of the method can be obtained by a brief summary of the first few experiments. After making oxygen, attention is drawn to its power to support combustion, its presence in air, relation between pure oxygen and air, rusting and its causes, and combustion in general, with the methods of testing and proving these facts, and some general broad deductions that can be drawn from a consideration of the phenomena observed. Hydrogen, chlorine, acids, bases, and salts, etc., are likewise treated in a simple, clear way, which with classroom exercises of equal value, cannot fail to awaken the interest of the student in the processes which are constantly in progress in nature. Another noteworthy feature is the extreme simplicity of the apparatus used, such as can be secured for a small sum and readily used where no special facilities for laboratory work are offered. These experiments are only printed on one side of the page, the blank leaf being intended for the records. This book can be used to great advantage in the lower grade schools, in most of which the sciences are now taught. J. E. G.

QUALITATIVE ANALYSIS FOR SECONDARY SCHOOLS. BY C. W. IRISH, A.B. (Harvard), Head Master of Lowell High School, Lowell, Mass. American Book Co. 1899. Price, 50 cents.

The author has attempted to prepare a book which can be used by secondary schools, and has introduced the simplest methods possible. The regular system of qualitative analysis, with some omissions of complex methods is adopted, and the principal reactions of each metal are given, and also some questions regarding its occurrence, compounds, etc., with equations representing some of the reactions which are to be filled out and balanced. J. E. G.

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CHEMICAL JOURNAL

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON ALKYL MALONIC NITRILES AND THEIR DERIVATIVES.

BY JOHN C. HESSLER.

Monalkylated derivatives of malonic nitrile were prepared by P. Henry,[1] in 1889, by the distillation of the corresponding alkyl cyanacetamides with phosphorus pentoxide, but, except the determination of a few physical constants, no study of them has yet been made.

The experiments described in this paper were carried out at the suggestion and under the direction of Prof. Nef. Their object was the preparation and study of certain alkyl malonic nitriles, their salts, and other derivatives. The substances specifically studied were ethyl and benzyl malonic nitriles; the former had been prepared by Henry.[2]

The synthesis of alkyl malonic nitriles requires the preparation of alkyl cyanacetic ethers, which will now be described.

Preparation of Crude Ethylcyanacetic Ether.

The product obtained by Henry[3] from cyanacetic ether and ethyl iodide by the Conrad-Limpach method was found to be a mixture of about 30 per cent. diethylcyanacetic ether and 70 per cent. monethylcyanacetic ether.

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[1] Henry: Jahresber., 1889, 637; Belg. Acad. Bull. [3], **18**, 670.

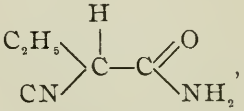
[2] Henry: *Ibid.*

[3] Henry: *Ibid.*

Fifty grams cyanacetic ether were mixed with 250 cc. absolute alcohol and treated with an alcoholic solution of 10.15 grams (1 atom) of sodium. 88 grams (1.25 molecules) of ethyl iodide were then added. The temperature rose to 40°, and within twenty minutes the solution was neutral to litmus. After the removal of the excess of alcohol and ethyl iodide by distillation water was added and the separated oil extracted with ether. The dried ether solution gave, on distillation, a substance boiling at 123°–124° at 50 mm., and at 206°–211° at ordinary pressure. The yield was 46 grams, or 74 per cent of the theoretical.

Thus prepared, crude ethylcyanacetic ether is a light and colorless oil, with an agreeable, ethereal odor. It is soluble in water to only a slight extent, but readily miscible with alcohol, benzene, and ether.

Sodium carbonate has no effect upon the substance, but aqueous sodium hydroxide dissolves it completely after several hours.

Ethylcyanacetamide,[1]  $\begin{array}{c}C_2H_5 \\ CN\end{array}\!\!>\overset{H}{\overset{|}{C}}-C\!\begin{array}{l}/\!\!/O \\ \backslash NH_2\end{array}$, was made by treating 20 grams crude ethylcyanacetic ether with 17.2 grams (2 molecules) of 28 per cent ammonia. After twenty-four hours the amide which had crystallized out was filtered off, and the mother liquor distilled at reduced pressure (24 mm.). The water, which distilled at 30°–35°, carried with it a small amount of a light oil; a considerable amount of the oil followed at 110°–112°, and, finally, a product boiling at 180°–190°, which solidified in the condenser. This was ethylcyanacetamide (weight 4.5 grams). The total yield of amide from 20 grams oil was 8.5 grams.

The substance boiling at 110°–112° was separated from the water in the usual manner, and found to be pure diethylcyanacetic ether (see below). Its weight was 4.5 grams.

Ethylcyanacetamide is an odorless solid, soluble in water and in alcohol, almost insoluble in ligroin and in ether, and crystallizing from alcohol in colorless right prisms, which melt at 113°. The substance distils at reduced pressure (180°–190° at 24 mm.) without decomposition, and sublimes at temperatures near its melting-point. Toward sodium carbonate it is indifferent, but it is readily dissolved by aqueous sodium hydroxide, with evolution of ammonia. A portion was recrystallized twice from alcohol, and dried in an air-bath at 80° and *in vacuo* over sulphuric acid.

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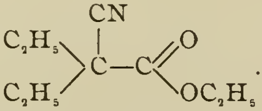
[1] Cf. Henry: *Ibid.*

A nitrogen determination gave the following result:

0.0804 gram gave 19 cc. N_2 at 25° C. and 742 mm.

	Calculated for C_5H_8NO.	Found.
N	25.00	25.04

Diethylcyanacetic Ether,[4]  $(C_2H_5)_2C(CN)—CO—OC_2H_5$.—As stated above, crude ethyl cyanacetic ether made by the Conrad-Limpach method (Henry) was found to contain a considerable amount of a substance apparently unaffected by standing twenty-four hours with a concentrated solution of ammonia. The behavior of the crude oil toward sodium hydroxide, which dissolves the greater portion in a few minutes, and the remainder only after several hours, also establishes the presence of a neutral product. Its amount is found by treating 5 grams of the crude oil in ethereal solution with caustic soda. 1.5 grams remain unaffected by the alkali. This neutral product, which was obtained in large quantity in the conversion of crude ethylcyanacetic ether into the amide (see above), now boils at 215°–216°. It was redistilled and an analysis made, the resulting figures agreeing with those required by diethylcyanacetic ether.

I. 0.1434 gram substance gave 0.3317 gram CO_2, and 0.1159 gram H_2O.

II. 0.2139 gram substance gave 16.2 cc N_2 at 25° and 745.6 mm.

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[1] Cf. Hesse: This JOURNAL, 18, 746.

	Calculated for $C_9H_{15}NO_2$.	Found. I.	II.
C	63.90	63.10	....
H	8.87	8.98	....
N	8.28	....	8.33

The substance is a colorless liquid, of pleasant odor, boiling at 215°–216°, and readily miscible with organic solvents, but insoluble in water. It is indifferent to sodium carbonate, but slowly soluble in caustic soda. After some months' standing, even in the dark, it becomes yellow.

Diethylcyanacetic ether was treated with 28 per cent ammonia and allowed to stand two weeks. The product was recrystallized from alcohol and found to melt at 122°. Hesse[1] gives the melting-point of diethylcyanacetamide as 120°. Diethylcyanacetic ether was heated with concentrated hydrochloric acid in a sealed tube to 100° C. The contents of the tube were diluted with water and extracted with ether. The acid product was removed by shaking with sodium carbonate, acidifying with dilute sulphuric acid, and extracting with ether. Distillation of the latter left an oil, of acid odor, which solidified *in vacuo* over sulphuric acid. This substance melted at 54°–56°, and re-melted at 56°. Hesse[2] gives the melting-point of diethylcyanacetic acid as 57°.

Persistent efforts were made to determine whether any cyanacetic ether was present in crude ethylcyanacetic ether, but not a trace of this substance could be found.

Henry[3] states that by several distillations of crude ethylcyanacetic ether he obtained a substance pure enough to be converted into amide, and that the vapor density and nitrogen determinations which he made gave figures that agreed with the theoretical. It is very unlikely, however, that he succeeded in effecting a complete separation, by fractional distillation, of diethylcyanacetic ether, boiling at 215°–216°, and ethylcyanacetic ether, boiling less than 10° lower. He states, further, that the ethylcyanacetic ether made by him was identical with that obtained by Haller[4] and by L. Henry[5] by the same method, and by Markownikow[6] from mercury and potassium cyanides and α-brombutyric ether.

[1] Cf. Hesse : *Ibid.*

[2] Hesse : *Ibid.*

[3] Henry : Belg. Acad. Bull. [3], **18**, 670.

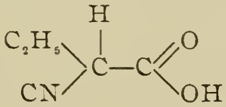
[4] Haller : Compt. rend., **104**, 1627.

[5] L. Henry : *Ibid.*, **104**, 1619.

[6] Markownikow : Ann. Chem. (Liebig), **182**, 330.

The mixed character of the product obtained by the action of cyanacetic ether and sodium alcoholate with ethyl iodide makes it probable that similar reactions carried out with other iodides always give mixtures of mono- and dialkylated cyanacetic ethers. For the same reason it seems unlikely that monalkylated malonic ethers have ever been obtained pure. The boiling-points of the substances are so close together that separation by fractional distillation is impossible, while the very slight differences in their composition prevent the detection in the monalkylated substances of small amounts of the dialkylated bodies.

Many similar cases have been observed and described, one of them by Nef[1] in his paper on acetoacetic ether derivatives.

Ethylcyanacetic Acid,  , was prepared by treating 18 grams of crude ethylcyanacetic ether in ethereal solution with aqueous sodium hydroxide, which leaves diethylcyanacetic ether intact. The alkaline solution was treated with an excess of dilute sulphuric acid and extracted with ether. Distillation of the ether left a slightly colored oil of acid odor, distilling undecomposed at reduced pressure (160°–161° at 24 mm.). The yield was 6 grams.

A nitrogen determination gave the following result:

0.1152 gram substance 13 cc. N_2 at 26° C. and 747.3 mm.

	Calculated for $C_5H_7NO_2$.	Found.
N	12.39	12.39

Ethylcyanacetic acid is a colorless, hygroscopic liquid with a faint odor, soluble in alcohol and in ether, and very soluble in water. At reduced pressure it distils without decomposition, but it is decomposed at ordinary pressures into carbon dioxide and butyronitrile, as is shown by the following experiment:

Three and four-tenths grams of the acid were heated in a flask to 170° C., at which temperature the substance decomposed into carbon dioxide and an oil boiling at 120°–140°.

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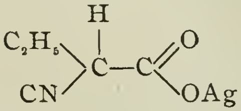
[1] Nef: *Ibid.*, **266**, 116–122.

Weight of oil, 2 grams. Redistilled, the oil boiled at 118°–120°, and had the characteristic odor and other properties of butyronitrile.

A brown liquid remained in the flask and solidified on cooling. This was soluble in sodium carbonate and precipitated by dilute sulphuric acid. Recrystallized from alcohol, the substance melted at 107°.5. It was undoubtedly slightly impure ethylmalonic acid (melting at 111°.5 when pure) formed by the saponification of some of the ethylcyanacetic acid.

Silver Salt of Ethylcyanacetic Acid,



$$\begin{matrix}C_2H_5\\CN\end{matrix}\!>\overset{\displaystyle H}{\overset{|}{C}}-C\begin{matrix}/\!\!/O\\ \backslash OAg\end{matrix}$$

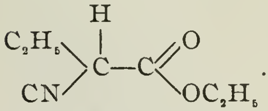
. — This substance was made by neutralizing ethylcyanacetic acid with ammonia and adding concentrated silver nitrate. The precipitated silver salt was washed with cold water and dried *in vacuo*. A silver determination, made by ignition of the substance, gave the following result :

0.1990 gram substance gave 0.0970 gram silver.

	Calculated for $C_5H_6NO_2Ag$.	Found.
Ag	49.09	48.74

The silver salt is crystalline and, at first, perfectly white, but colors slowly in the light. The vapor that escapes when the substance is heated has the odor of butyronitrile.

Preparation of Pure Ethylcyanacetic Ether,



$$\begin{matrix}C_2H_5\\CN\end{matrix}\!>\overset{\displaystyle H}{\overset{|}{C}}-C\begin{matrix}/\!\!/O\\ \backslash OC_2H_5\end{matrix}$$

.—36 grams (about 3 molecules) of ethyl iodide were treated in a flask provided with a reversed condenser with 16.5 grams of the silver salt of ethylcyanacetic acid. Interaction took place on heating to 50°–55°, and 9.5 grams, *i. e.* 90 per cent of the theory, of ethylcyanacetic ether, boiling at 207°–209°, were obtained. To insure the removal of all ethyl iodide the product was heated with about 1 gram of silver ethylcyanacetate, and then redistilled.

An analysis gave the following results:

0.2018 gram substance gave 0.4430 gram CO_2, and 0.1428 gram H_2O.

	Calculated for $C_7H_{11}NO_2$.	Found.
C	59.57	59.86
H	7.80	7.86

Pure ethylcyanacetic ether is a colorless oil having a faint, sweet odor, noticeably different from that of the crude substance obtained by the Conrad-Limpach method. Its specific gravity at 22°.3 is 0.985.

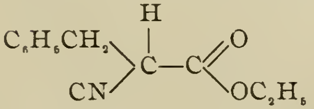
Action of Dry Sodium Cyanacetic Ether with Ethyl Iodide.

It seemed possible that the formation of the relatively large amount of diethylcyanacetic ether obtained in the Conrad-Limpach reaction was due to the presence of alcohol, and that, if dry sodium cyanacetic ether were treated with ethyl iodide, the amount of dialkylated substance might be considerably diminished. This proved to be the fact.

Dry sodium cyanacetic ether was prepared by adding sodium wire to a solution of cyanacetic ether in absolute ether. The yield of dry salt was regularly 95 per cent of the theory. 15 grams of sodium cyanacetic ether were heated in a sealed tube to 100° with 17.3 grams (1 molecule) of ethyl iodide and 10 cc. absolute ether. The contents of the tube were treated with water, and extracted with ether. Distillation of the ether left an oil boiling at 207°–209°, which had all the properties of crude ethylcyanacetic ether. Yield, 12 grams. Treatment with caustic soda showed that the product contained 1.5 grams, *i. e.* 12.5 per cent, of diethylcyanacetic ether. This method does not, therefore, avoid the formation of the dialkylated body, although it reduces its amount.

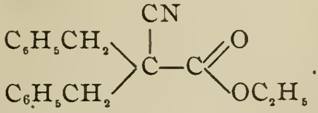
Action of Cyanacetic Ether with Alcoholic Sodium Ethylate and Benzyl Chloride.

Mono- and Dibenzylcyanacetic Ethers,



$$\left.\begin{matrix} C_6H_5CH_2 \\ CN \end{matrix}\right> \overset{H}{\overset{|}{C}} - C \begin{matrix} \nearrow O \\ \searrow OC_2H_5 \end{matrix}$$

and



$$\left.\begin{matrix} C_6H_5CH_2 \\ C_6H_5CH_2 \end{matrix}\right> \overset{CN}{\overset{|}{C}} - C \begin{matrix} \nearrow O \\ \searrow OC_2H_5 \end{matrix}$$

.—

Judging from the results obtained in the preparation of ethylcyanacetic ether by the Conrad-Limpach method it seemed very likely that an attempt to prepare benzylcyanacetic ether by the same method would likewise give a mixture of products.

Cassirer,[1] who was the first to carry out this experiment, states that he obtained from equimolecular quantities of cyanacetic ether, benzyl chloride, and sodium ethylate a heavy oil, which was saponified by alcoholic caustic potash to dibenzylcyanacetic acid. He seems to have overlooked entirely the small amount of monobenzylcyanacetic ether formed.

The experiment was carried out as follows: 20 grams cyanacetic ether, dissolved in absolute alcohol, were treated with an alcoholic solution of 4.07 grams (1 atom) of sodium, and with 22.4 grams (1 molecule) of benzyl chloride. The mixture was warmed on a water-bath for fifteen minutes, and found to be neutral to litmus. The alcohol having been distilled off, the residue was treated with water, extracted with ether, and the ethereal solution dried with calcium chloride. Distillation of the ether left a dark oil, which was distilled at reduced pressure (21 mm.), the fractions obtained boiling as follows: 1. below 78°; 2. 78°–128°; 3. 178°–238°. The first fraction consisted of alcohol and benzyl chloride, the second of benzyl chloride and a very small amount of cyanacetic ether, and the third of a colorless liquid boiling at 176°–183° at 21 mm., and a viscous, yellow liquid boiling at 234°–236° at the same pressure. These two substances were mono- and dibenzylcyanacetic ethers, respectively (see below). The yield of the former was only 2–3 grams, that of the latter 10–12 grams.

Owing to the fact that so small an amount of monobenzylcyanacetic ether was formed by the Conrad-Limpach method, it seemed better to treat dry sodium cyanacetic ether with benzyl chloride.

Action of Dry Sodium Cyanacetic Ether with Benzyl Chloride.

Twenty-seven grams of sodium cyanacetic ether were mixed in a flask with 25 grams (1 molecule) of benzyl chloride, and heated gently. Reaction began at 65°, and was complete at 80°. The product was treated with water, and the separated oil extracted with ether. The residue remaining after the evaporation of the ether was distilled at reduced pressure (20 mm.) in fractions boiling as follows:

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[1] Cassirer: Ber. d. chem. Ges., **25**, 3028.

Fraction.	Temperature.	Weight. Grams.
1	65°–76°	7.8
2	76°–120°	4.2
3	165°–210°	11.3
4	210°–233°	6.0

The first fraction consisted of benzyl chloride. The second was separated, by treatment with aqueous alkali, into benzyl chloride and an oil which crystallized on standing over sulphuric acid, melted at 66°–67°, and had the other properties of cyanacetic acid. Cyanacetic ether was, therefore, present in the second fraction.

The third portion was redistilled at reduced pressure (20 mm.) and found to boil chiefly at 176°–183°. It had all the properties of the corresponding fraction obtained by the Conrad-Limpach method. The oil boiling at 176°–183° was again distilled at 20 mm., and the portion boiling at 176° was analyzed, with the following results:

I. 0.1758 gram substance gave 0.4557 gram CO_2, and 0.1044 gram H_2O.

II. 0.2075 gram substance gave 13.1 cc. N_2 at 22° and 741.5 mm.

	Calculated for $C_{12}H_{13}NO_2$.	Found. I.	Found. II.
C	70.93	70.69	....
H	6.40	6.59	....
N	6.90	....	7.03

Three preparations, aggregating 42 grams of sodium cyanacetic ether, gave 16.4 grams of oil boiling at 165°–210° at 21 mm., from which 13.3 grams of almost pure benzylcyanacetic ether, boiling at 176°–185° at 21 mm., were obtained. Benzylcyanacetic ether is a colorless, limpid oil, having a faint aromatic odor. It is insoluble in water, but readily miscible with organic solvents. Toward sodium carbonate the substance is indifferent, but it reacts instantly with caustic soda, forming the sodium salt of benzylcyanacetic acid. If the alkaline solution is heated, ammonia is given off and the sodium salt of benzylmalonic acid is formed. With 28 per cent ammonia, benzylcyanacetic ether reacts at once, forming benzylcyanacetamide.

The highest boiling fraction (4) obtained by heating dry sodium cyanacetic ether with benzyl chloride (see above) was redistilled at reduced pressure (20 mm.), and the portion boiling above 230° was treated in ethereal solution with aqueous sodium hydroxide, to remove any benzylcyanacetic ether which might be present. Distillation of the ether left a yellow oil boiling at 237° at 25 mm. Several attempts to solidify it proving unsuccessful, the substance was analyzed as a thick syrup, which had all the properties of the corresponding product obtained by the Conrad-Limpach method.

The analysis gave the following figures :

I. 0.4015 gram substance gave 1.1349 grams CO_2, and 0.2334 gram H_2O.

II. 0.1270 gram substance gave 0.3606 gram CO_2, and 0.0741 gram H_2O.

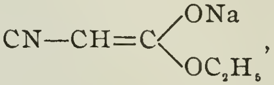
III. 0.5680 gram substance gave 24.6 cc. N_2 at 22° C. and 747 mm.

	Calculated for $C_{19}H_{19}NO_2$.	Found. I.	II.	III.
C	77.81	77.09	77.44	....
H	6.48	6.46	6.48	....
N	4.78	....	....	4.83

Dibenzylcyanacetic ether, obtained and analyzed as just described, in the form of a thick, viscous, yellow syrup, solidified after several weeks, forming large, colorless crystals, melting at 33°. The substance is insoluble in water and indifferent toward aqueous alkalies, but dissolves readily in alcohol and in ether.

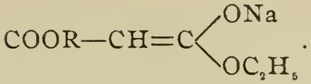
Constitution of Sodium Cyanacetic Ether.

The work of Nef on acetoacetic ether, malonic ether, the nitroparaffins, etc., proves that the metallic salts formed by these compounds have the metal bound to oxygen. By analogy, sodium cyanacetic ether must have the constitution,



$$CN{-}CH{=}C\begin{cases}ONa\\OC_2H_5\end{cases}, \qquad (I)$$

like that of sodium malonic ether,



$$\mathrm{COOR{-}CH{=}C}\begin{matrix}\diagup \mathrm{ONa} \\ \diagdown \mathrm{OC_2H_5}\end{matrix}.$$

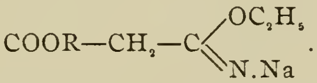
In connection with his experiments on cyanogen and isocyanogen compounds, Nef[1] was led to the consideration of another possible formula for the salt, namely,

$$\mathrm{COOC_2H_5{-}CH{=}C{=}N.Na.} \qquad \text{(II)}$$

A salt of this constitution could indeed be formed by addition of sodium ethylate to the cyanogen group of the free cyanacetic ether,

$$\mathrm{COOR{-}CH_2{-}C} \vdots \mathrm{N},$$

and subsequent loss of alcohol from the resulting addition-product,

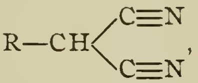


$$\mathrm{COOR{-}CH_2{-}C}\begin{matrix}\diagup \mathrm{OC_2H_5} \\ \diagdown\!\!\diagdown \mathrm{N.Na}\end{matrix}.$$

The formation of salts in the case of malonic nitrile,

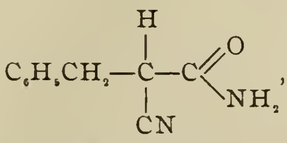
$$\mathrm{CN{-}CH_2{-}C{\equiv}N},$$

and its monalkylated substitution-products,



$$\mathrm{R{-}CH}\begin{matrix}\diagup \mathrm{C{\equiv}N} \\ \diagdown \mathrm{C{\equiv}N}\end{matrix},$$

does, in all probability, take place in this manner. The facts known at present, however, in regard to cyanacetic ether, point conclusively to formula (I) as representing the constitution of its sodium salt. Caustic alkalies and dilute acids convert the substance into cyanacetic acid, and ammonia forms with it cyanacetamide, in each of which substances the cyanogen group is unquestionably intact. This shows that the carbethoxy and not the cyanogen group is the point of attack when cyanacetic ether is treated with reagents. The same statement holds good in the case of its monalkylated substitution-products.

Benzylcyanacetamide,  $\mathrm{C_6H_5CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}}{-}C}\begin{matrix}\diagup\!\!\diagup \mathrm{O} \\ \diagdown \mathrm{NH_2}\end{matrix}$, was prepared

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[1] Nef: Ann. Chem. (Liebig), 287, 281.

from pure benzylcyanacetic ether by treatment with a 28 per cent solution of ammonia. After twenty-four hours the crystalline mass was filtered off, washed with water, and recrystallized from alcohol.

An analysis resulted as follows :

I. 0.1980 gram substance gave 0.4990 gram CO_2, and 0.1036 gram H_2O.

II. 0.1007 gram substance gave 14.6 cc. N_2 at 22° C. and 744.2 mm.

	Calculated for $C_{10}H_{10}N_2O$.	Found. I.	II.
C	68.96	68.74	....
H	5.74	5.81	....
N	16.09	....	16.16

For the preparation of benzylcyanacetamide in quantity it is much more economical to treat crude benzylcyanacetic ether, boiling at 165°–210° at 20 mm., directly with ammonia, and to free the product from a small amount of adhering dibenzylcyanacetic ether by recrystallization from alcohol. In this way it is possible to obtain about 15 grams of the amide from 50 grams of sodium cyanacetic ether.

Benzylcyanacetamide crystallizes from alcohol in large, colorless, right prisms melting at 130°, and from water in white needles. In ligroin and in ether it is only slightly soluble. Toward sodium carbonate the substance is indifferent, but sodium hydroxide dissolves it readily, even at the ordinary temperature, evolving ammonia, and forming the sodium salt of benzylcyanacetic acid (see below). At reduced pressure benzylcyanacetamide distils with little or no decomposition.

Action of Phosphorus Pentachloride upon Benzylcyanacetamide.

Benzylmalonic Nitrile, $C_6H_5CH_2CH(CN)_2$.—4.4 grams benzylcyanacetamide and 2.1 grams phosphorus pentachloride were mixed in a flask having a receiver, and the flask was exhausted to 20 mm., and heated. At 74° the mixture began to melt and to give off hydrochloric acid gas. The temperature was raised gradually until there was quiet fusion and the contents of the flask distilled over into the receiver. The yield of distillate, which solidified at once, was 3.2 grams, or 84 per cent of the theory. The proportions of benzylcyanacetamide and of phosphorus pentachloride taken, correspond to 5 molecules of the former and 2 of the latter, similar proportions of cyanacetamide and of the pentachloride having been found by Hesse[1] to give the best yield of malonic nitrile. The substance was recrystallized from alcohol and dried over sulphuric acid.

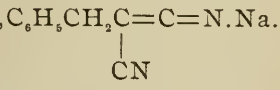
An analysis gave the following results:

I. 0.1356 gram substance gave 0.3828 gram CO_2, and 0.0641 gram H_2O.

II. 0.1084 gram substance gave 17.5 cc. N_2 at 20°.5 C. and 739.1 mm.

	Calculated for $C_{10}H_8N_2$.	Found. I.	II.
C	76.92	76.99	....
H	5.13	5.25	....
N	17.95	....	17.99

Benzylmalonic nitrile is soluble in alcohol, ether, benzene, and acetic ether; sparingly soluble in ligroin (70°–80°) and in water. From alcohol it crystallizes in large, white rhombohedra melting at 91°; from ligroin and from water in long needles. The substance distils undecomposed at reduced pressure (174° C. at 23 mm.). Caustic soda dissolves the dry solid and extracts it from its ethereal solution. If the alkaline solution is poured at once into dilute acids, benzylmalonic nitrile is regenerated; if allowed to stand twenty-four hours at the ordinary temperature, ammonia is evolved, and the sodium salt of benzylcyanacetic acid is formed; if heated, more ammonia is given off, and the solution then contains the sodium salt of benzylmalonic acid.

Sodium Salt of Benzylmalonic Nitrile, 

$C_6H_5CH_2\underset{\substack{| \\ CN}}{C}{=}C{=}N.Na.$

—This substance was prepared by treating 4 grams of benzylmalonic nitrile in absolute benzene solution with 0.6 gram (a slight excess) of sodium. Only slight action taking place at the ordinary temperature, the mixture was warmed and allowed to stand over night. The precipitated sodium salt was washed with benzene, and dried *in vacuo* over sulphuric acid. The yield was 3.5 grams, or 78 per cent of the theory.

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[1] Hesse: This Journal, 18, 726.

A sodium determination resulted as follows:

0.2106 gram substance gave 0.0860 gram Na_2SO_4.

	Calculated for $C_{10}H_7N_2Na$.	Found.
Na	12.92	13.22

The salt is an almost white, amorphous powder, which absorbs moisture from the air, and then becomes dark and undergoes decomposition. Poured into dilute acids, the substance regenerates benzylmalonic nitrile in the form of a white, bulky precipitate. The salt was dissociated into benzylmalonic nitrile and sodium hydroxide on addition of water; on standing twenty-four hours most of the precipitated benzylmalonic nitrile redissolved, but a small amount remained undissolved after three days. This was accordingly filtered off, dried, and found to melt at 130°. When it was mixed with pure benzylcyanacetamide the melting-point of the latter was not lowered. The substance was, therefore, taken to be benzylcyanacetamide, formed by the addition of water to benzylmalonic nitrile. The filtrate contained the sodium salt of benzylcyanacetic acid, as was proved by acidifying with dilute sulphuric acid and extracting with ether. Evaporation of the ether left a substance melting at 101°–102° when purified, and identical in every respect with benzylcyanacetic acid (see below).

Behavior of Sodium Benzylmalonic Nitrile when Heated.—4 grams of the sodium salt were heated in a flask, and began to decompose at 120° C. At higher temperatures the substance swelled up to a black mass several times its original bulk. The flask was accordingly exhausted to 20 mm. and carefully heated. As a result 0.7 gram of an oil, boiling at 120°–140° at the reduced pressure, was obtained. Hot water extracted from the black residue a substance which was precipitated as a slimy, brown solid on the addition of dilute nitric acid. This proved to be the so-called azulmic acid. A strong odor of prussic acid was noticed in the filtrate from the azulmic acid. Silver nitrate was therefore added, and a precipitate of silver cyanide obtained. Its amount corresponded to 0.4-0.5 gram of sodium cyanide, or 36–45 per cent of the theory.

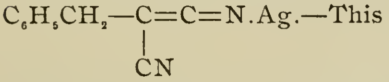
The oil boiling at 120°–140° was redistilled and analyzed with the following results :

I. 0.1222 gram substance gave 0.3724 gram CO_2, and 0.0763 gram H_2O.

II. 0.1401 gram substance gave 13.65 cc. N_2 at 16° C. and 743.5 mm.

	Calculated for C_9H_9N.	Found. I.	II.
C	82.44	83.06	....
H	6.87	6.94	....
N	10.69	....	11.14

The figures obtained agree fairly well with those calculated for hydrocinnamic nitrile.[1] That the oil was actually this substance was proved by its conversion into hydrocinnamic acid when heated in a sealed tube with concentrated hydrochloric acid.



$\underset{\displaystyle CN}{C_6H_5CH_2—\overset{}{C}}=C=N.Ag$

Silver Salt of Benzylmalonic Nitrile, $C_6H_5CH_2—C(CN)=C=N.Ag$.—This substance was made by the method of Comstock and Kleeberg[2] and Tafel and Enoch.[3]

To a cold solution of 1.56 grams benzylmalonic nitrile in 150 cc. 66 per cent alcohol were added 1.7 grams (1 molecule) of silver nitrate in concentrated aqueous solution, and then, drop by drop, the calculated amount of half-normal caustic potash. A bulky, amorphous, white precipitate was formed, which was thoroughly washed by decantation with water, and dried *in vacuo* over sulphuric acid. The yield was 2.4 grams, or 90 per cent of theory.

A silver determination gave the following result :

0.1724 gram substance gave 0.0710 gram Ag.

	Calculated for $C_{10}H_7N_2Ag$.	Found.
Ag	41.06	41.18

The silver salt can be kept indefinitely *in vacuo* over sulphuric acid, but in the air, even when protected from the light, it soon becomes black, and emits an odor like that of hydrocinnamic nitrile. When the salt is treated with dilute nitric acid, benzylmalonic nitrile is regenerated. Methyl and ethyl iodides react instantly with the substance. Heated, it begins to decompose at 80°, and at higher temperatures becomes a hard, black mass. Ether then extracts some tarry material, and leaves a gray substance having the properties of silver cyanide. The dissociation of the silver salt of benzylmalonic nitrile into silver cyanide, and that of the sodium salt into sodium cyanide makes it very probable that their constitution is to be represented by the formula

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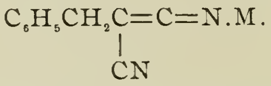
[1] Cf. Hoffman : Ber. d. chem. Ges., **7**, 520.

[2] Comstock and Kleeberg : This JOURNAL, **12**, 498.

[3] Tafel and Enoch : Ber. d. chem. Ges., **23**, 104.



$$C_6H_5CH_2\underset{\displaystyle CN}{\underset{|}{C}}=C=N.M.$$

Assuming with Nef[1] that the double cyanides and fulminates and the double salts of isonitriles with cyanide of silver[2] have the constitution :

$$AgNC : CNK ;$$
$$AgONC : CNOK ;$$
$$RNC : CNAg,$$

it will be seen that the monalkylated malonic nitrile salts have an analogous constitution. Since Gautier has proved that potassium cyanide sets free the isonitrile from its double salt,

$$RNC : CNAg,$$

it was hoped that the silver salt of benzylmalonic nitrile might dissociate in an analogous manner. An experiment carried out with this object in view resulted as follows :

Silver benzylmalonic nitrile (3 grams) was added to aqueous potassium cyanide. The solution obtained was filtered from a white, insoluble substance, and treated with dilute nitric acid. This produced a precipitate of silver cyanide weighing 1.2 grams, or 80 per cent of the theory. The substance insoluble in the solution of potassium cyanide melted at 90° when recrystallized from ligroin, and had the other properties of benzylmalonic nitrile. Its weight was 1.1 grams, or 68 per cent of the theory. That this substance was actually benzylmalonic nitrile was proved by two nitrogen determinations, which gave the following results :

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[1] Ann. Chem. (Liebig), **298**, 313. This question is being investigated experimentally in this laboratory and will include a study of the ferro- and the ferricyanides. J. U. NEF.

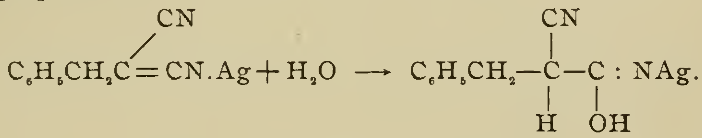
[2] Gautier : Ann. chim. phys. [4], **17**, 203.

I. 0.1601 gram substance gave 25.4 cc. N_2 at 19°.5 C. and 738.5 mm.

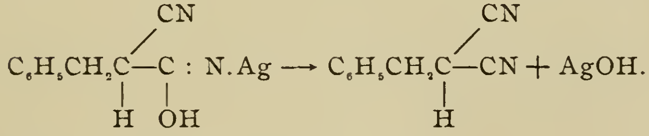
II. 0.0984 gram substance gave 16 cc. N_2 at 23°.5 C. and 738.1 mm.

	Calculated for $C_{10}H_8N_2$.	Found.	
		I.	II.
N	17.95	17.75	17.84

The action of potassium cyanide seems therefore to be a simple hydrolysis, and is probably represented by the following equations :

1. 

$$C_6H_5CH_2\overset{CN}{C}{=}CN.Ag + H_2O \longrightarrow C_6H_5CH_2-\underset{H}{\overset{CN}{C}}-\underset{OH}{C}:NAg.$$

2. 

$$C_6H_5CH_2\underset{H}{\overset{CN}{C}}-\underset{OH}{C}:N.Ag \longrightarrow C_6H_5CH_2\underset{H}{\overset{CN}{C}}-CN + AgOH.$$

3. $AgOH + KNC \longrightarrow AgNC + KOH.$

Ethylmalonic Nitrile,[1] $C_2H_5-CH(CN)_2$.—5.6 grams of dry ethylcyanacetamide and 4.2 grams of phosphorus pentachloride were thoroughly mixed in a flask having a receiver. The apparatus was exhausted to 26 mm., and heat applied. The reaction took place at 80°, the mixture melted and became dark-colored, and hydrochloric acid gas came off in large quantities. The temperature was then raised very gradually to 100° or above, the end of the reaction being indicated by a violent frothing. This having ceased, the ethylmalonic nitrile formed distilled over at 90°–107°. The yield was 4 grams, or 85 per cent of the theory.

To free the product from any phosphorus oxychloride and ethylcyanacetamide which it might contain, it was shaken with water, dried, and redistilled.

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[1] Cf. Henry : Jahresber., 1889, 637.

An analysis gave the following figures :

I. 0.1628 gram substance gave 0.3772 gram CO_2, and 0.0976 gram H_2O.

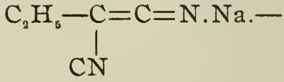
II. 0.1171 gram substance gave 0.2721 gram CO_2, and 0.0684 gram H_2O.

III. 0.1511 gram substance gave 39.2 cc. N_2 at 16° C. and 747.6 mm.

	Calculated for $C_5H_6N_2$.	Found. I.	II.	III.
C	63.83	63.20	63.38	....
H	6.38	6.65	6.49	....
N	29.79	....	....	29.85

Ethylmalonic nitrile is a light, colorless oil, only slightly soluble in water, but readily soluble in ether and in alcohol. Its odor is faint, and resembles that of acetamide. The substance boils at 90°–91° at 20 mm., and at 200° at the ordinary pressure (746 mm.). After a few weeks, even when kept in the dark, the oil becomes brown. It is indifferent to sodium carbonate, but dissolves readily in sodium hydroxide at the ordinary temperature with evolution of ammonia and formation of the sodium salt of ethylcyanacetic acid. If the alkaline solution is heated, more ammonia is evolved, and the sodium salt of ethylmalonic acid is formed.

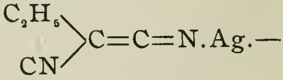
Sodium Salt of Ethylmalonic Nitrile,



$C_2H_5-\underset{\displaystyle CN}{\underset{|}{C}}=C=N.Na.$—

An ethereal solution of ethylmalonic nitrile does not react appreciably with metallic sodium even after two or three hours. If a drop of absolute alcohol is added, vigorous action begins, and an oil separates out which is insoluble in ether. A solution of ethylmalonic nitrile in pure benzene likewise reacts only very slightly with metallic sodium, even at the boiling-point of benzene. When the mixture was allowed to stand several days, however, a small amount of a slightly colored, amorphous powder was obtained. This was dried *in vacuo* over sulphuric acid, but decomposed so readily on exposure to the air that no further study of it was attempted.

Silver Salt of Ethylmalonic Nitrile,[1]



$\begin{matrix}C_2H_5\\CN\end{matrix}\!\!>C=C=N.Ag.$—

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[1] Cf. Henry : *Ibid.*

This substance was prepared in the same way as the silver salt of benzylmalonic nitrile, but greater precautions were taken to keep the temperature low.

Five grams ethylmalonic nitrile, dissolved in 50 per cent alcohol, were treated with an aqueous solution of 9 grams (1 molecule) of silver nitrate, and then with the calculated amount of a half-normal solution of caustic potash. During the addition of the alkali the mixture was kept cold by the introduction of pieces of ice, and was shaken vigorously. The amorphous, white precipitate of silver salt was washed by decantation with cold water, collected upon a filter, dried from five to ten minutes upon a clay plate, and then over concentrated sulphuric acid. Although the operations just described were carried out in a room at 2° C., the substance invariably decomposed after fifteen to twenty minutes. The decomposition was accompanied by a marked evolution of heat, and the bulky, white salt became black, pasty, and of small volume; at the same time water and an oil separated from the mass. The water held in solution a substance having an acid reaction and an odor like that of acetic or propionic acid. Ether and benzene extracted from the decomposed silver salt a small amount of a yellow oil, which was almost insoluble in water, but soluble in sodium carbonate and in sodium hydroxide. When these solutions were acidified the substance was apparently regenerated, but it could not be distilled without decomposition. Some of the oil was left standing several days, and deposited a white, crystalline solid melting at 134°. The amount of this substance was, however, so small that it was not examined further.

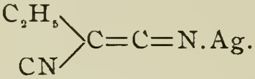
The black mass which had been treated with ether and with benzene was washed with hot alcohol and with water, and, finally, to free it from metallic silver, with dilute nitric acid. The residue thus obtained was a light gray, amorphous solid having the properties of silver cyanide. Heated, it was decomposed into silver and cyanogen, as is shown by the following results, which were obtained from independent preparations of silver ethylmalonic nitrile:

I. 0.3548 gram substance gave 0.2758 gram Ag.
II. 0.0845 gram substance gave 0.0658 gram Ag.
III. 0.0989 gram substance gave 0.0775 gram Ag.

	Calculated for AgNC.	Found. I.	II.	III.
Ag	80.59	77.73	77.87	78.36

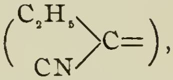
A small amount of tarry material, which adhered to the silver cyanide and escaped only upon ignition, was, no doubt, the cause of the low results.

In the case of the silver salt of ethylmalonic nitrile, as in that of the silver salt of benzylmalonic nitrile, all attempts to get both organic residues failed. Yet the spontaneous dissociation of these salts into silver cyanide, the formula of which has been determined by Nef[1] to be Ag—N=C, makes it extremely probable that in them the metal is bound to nitrogen. The formula of silver ethylmalonic nitrile is, therefore, written



$$\begin{matrix} C_2H_5 \\ CN \end{matrix} > C{=}C{=}N.Ag.$$

Loss of silver cyanide must leave a residue,



$$\left(\begin{matrix} C_2H_5 \\ CN \end{matrix} > C{=} \right),$$

capable, no doubt, of oxidation and of polymerization, thus giving rise to a complex mixture of substances.

Most persistent efforts were made in the instance described above to determine the nature of these products. The amount of material used was inadequate for this purpose, but the work done established unquestionably their complex character.

The only positive results obtained, therefore, show that salts of monalkylated malonic nitriles dissociate into metallic isocyanides, M—N=C. In the case of silver ethylmalonic nitrile this takes place spontaneously at 0°, with silver benzylmalonic nitrile at 80°, and with the corresponding sodium salt at 120°.

Action of Malonic Nitrile with Alcoholic Sodium Ethylate and Benzyl Chloride.

Dibenzylmalonic Nitrile $(C_6H_5CH_2)_2{=}C{=}(CN)_2$.—3 grams malonic nitrile (made by the method of Hesse[1] from cyanacetamide and phosphorus pentachloride) were dissolved in absolute alcohol, and treated with an alcoholic solution of 1.05 grams (1 atom) of sodium, and with 5.75 grams (1 molecule) of benzyl chloride. The temperature of the mixture rose to 40°, and common salt was precipitated. On cooling, long, white crystals of dibenzylmalonic nitrile (see below) were deposited. These were filtered off and washed with water to free them from sodium chloride. The alcoholic filtrate left, on distillation, a white, crystalline mass. This was treated with hot water, in which dibenzylmalonic nitrile is insoluble, and a small amount of monobenzylmalonic nitrile obtained. The total yield of product was 3.6 grams, fully 90 per cent of this amount being dibenzylmalonic nitrile.

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[1] Nef: Ann. Chem. (Liebig), **287**, 265-359.

An analysis of this substance gave the following results:

I. 0.1372 gram substance gave 0.4128 gram CO_2, and 0.0716 gram H_2O.

II. 0.1558 gram substance gave 16.4 cc. N_2 at 24° and 741.8 mm.

	Calculated for $C_{17}H_{14}N_2$.	Found. I.	Found. II.
C	82.93	82.07	....
H	5.69	5.79	....
N	11.38	....	11.58

Dibenzylmalonic nitrile is a white, crystalline solid melting at 131°. It dissolves in hot alcohol and in ether, is slightly soluble in hot ligroin, and insoluble in water. Toward aqueous alkalies, even when hot, it is entirely indifferent.

Action of Dry Sodium Malonic Nitrile with Benzyl Chloride.

Dry sodium malonic nitrile, made according to the method of Schmidtmann,[2] was heated in a flask with the calculated amount of benzyl chloride with the expectation that a relatively larger amount of monobenzylmalonic nitrile than that produced by the Conrad-Limpach method might be formed. The reaction, accompanied by much charring, took place at 90°. The dark product was treated with boiling ligroin several times, and a white, crystalline substance obtained, which proved to be a mixture of mono- and dibenzylmalonic nitriles. Its amount was, however, very small. A similar result was obtained by heating dry sodium malonic nitrile with benzyl chloride and absolute ether in a sealed tube at 150° C.

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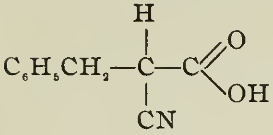
[1] Hesse: This Journal, 18, 723.

[2] Schmidtmann: Ber. d. chem. Ges., 29, 1171.

Benzylcyanacetic Acid (*α-Cyan-β-phenylpropionic Acid*),



$C_6H_5CH_2-\overset{H}{\underset{CN}{C}}-C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown OH}$.—This substance was prepared by treating crude benzylcyanacetic ether in ethereal solution with aqueous sodium hydroxide and adding the alkaline solution to an excess of dilute sulphuric acid. The separated oil was extracted with ether, the ether dried, and distilled. The acid was thus obtained as a liquid, which solidified when cooled. It was recrystallized from benzene and an analysis made, with the following results:

I. 0.1140 gram substance gave 0.2856 gram CO_2, and 0.0543 gram H_2O.

II. 0.2068 gram substance gave 15 cc. N_2 at 20°.5 C. and 741.6 mm.

	Calculated for $C_{10}H_9NO_2$.	Found. I.	II.
C	68.59	68.33	....
H	5.14	5.29	....
N	8.00	....	8.11

Benzylcyanacetic acid is a white, crystalline solid, melting at 101°–102°, soluble in benzene, alcohol, and ether, and somewhat soluble in water. Hot caustic soda saponifies it, forming benzylmalonic acid. The substance cannot be distilled at ordinary pressure, since it decomposes into carbon dioxide and hydrocinnamic nitrile, as is shown by the following experiment:

Two and a half grams of the acid were heated in a flask to 170°–200°, carbon dioxide being evolved in large quantities. The residue in the flask was then dissolved in ether, the ethereal solution shaken with sodium carbonate, and dried with chloride of calcium. The ether left, on evaporation, an oil boiling at 253°; weight, 1 gram, or 53 per cent of the theory. That this substance was hydrocinnamic nitrile was proved by heating it in a sealed tube with concentrated hydrochloric acid; hydrocinnamic acid, melting at 47°–48°, was thus formed.

Silver Salt of Benzylcyanacetic Acid, $C_6H_5CH_2CHCNCOOAg$.—This substance was prepared as follows: The acid was dissolved in ammonia, and the excess of the latter removed over sulphuric acid. The white ammonium salt, which had crystallized out, was redissolved in water and treated with a concentrated solution of silver nitrate. The silver salt was thus obtained as an amorphous, white precipitate, which became crystalline on standing. It was washed with water and dried over sulphuric acid. An analysis gave the following results:

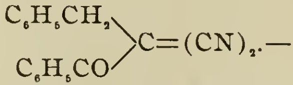
I. 0.1270 gram substance gave 0.0480 gram Ag.

II. 0.0882 gram substance gave 0.0337 gram Ag.

	Calculated for $C_{10}H_8NO_2Ag$.	Found.	
		I.	II.
Ag	38.29	37.80	38.21

The silver salt is precipitated, also, when concentrated silver nitrate is added directly to a concentrated aqueous solution of the acid. It is a heavy, white solid, which darkens slowly in the light. Heated to 140° it melts with decomposition, giving off a vapor having the odor of hydrocinnamic nitrile.

Benzoylbenzylmalonic Nitrile,



$$\begin{matrix} C_6H_5CH_2 \\ C_6H_5CO \end{matrix}\!\!>\!C{=}(CN)_2$$

.—2.7 grams of benzoyl chloride, dissolved in 20 cc. absolute ether, were treated in the cold with 3.4 grams (1 molecule) of sodium benzylmalonic nitrile. After twenty-four hours the benzoylbenzylmalonic nitrile was obtained as a crystalline mass. The substance was separated from the sodium chloride by means of boiling ether, recrystallized once from ether, and dried *in vacuo* over sulphuric acid. Yield 3 grams, or 60 per cent of the theory. A nitrogen determination gave the following result:

0.1579 gram substance gave 15.4 cc. N_2 at 19°.5 C. and 743.6 mm.

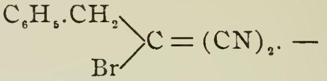
	Calculated for $C_{17}H_{12}N_2O$.	Found.
N	10.77	10.99

Thus prepared, benzoylbenzylmalonic nitrile is a perfectly white, crystalline solid, melting at 100°, sparingly soluble in hot ligroin (70°–80°), and readily soluble in warm ether. It is unaffected by water and by sodium carbonate, but is decomposed by hot alcohol and by aqueous caustic soda, as is established by the following experiments :

a. The substance was heated for half an hour with absolute alcohol in a flask provided with a reversed condenser. Distillation of the alcohol left an oil from which a white, crystalline solid was deposited. The crystal-form and the melting-point (91°) of the solid proved it to be benzylmalonic nitrile. The oil was readily identified as benzoic ether.

b. An ethereal solution of benzoylbenzylmalonic nitrile was treated with caustic soda and the alkaline solution poured at once into dilute sulphuric acid. The product was a mixture of benzoic acid and benzylmalonic nitrile , these were separated by treatment with sodium carbonate, and thoroughly identified.

Brombenzylmalonic Nitrile,



$$\begin{matrix} C_6H_5.CH_2 \\ Br \end{matrix} \Big> C = (CN)_2.$$

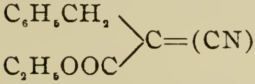
— This substance was prepared by adding 2 grams of sodium benzylmalonic nitrile to an absolute ethereal solution of 1.8 grams (2 atoms) of bromine. After twenty-four hours water was added to dissolve the sodium bromide formed, and the ethereal solution was treated with caustic soda, to insure removal of benzylmalonic nitrile. Distillation of the ether left a slightly colored solid, which was boiled, in ligroin solution, with boneblack, and thus obtained perfectly white. A portion, recrystallized from a mixture of absolute ether and ligroin (40°–60°), gave the following results on analysis :

I. 0.1713 gram gave 18.3 cc. N_2 at 20°.5 and 748.2 mm.
II. 0.0760 gram contained 0.02582 gram Br.

	Calculated for $C_{10}H_7N_2Br$.	Found. I.	II.
N	11.91	12.05	....
Br	34.04	....	33.97

The substance dissolves readily in ether, but is difficultly soluble in water. It crystallizes from alcohol in thin plates with serrated edges, and from ligroin in fine needles, melting in each case at 119°–120°. Unlike the benzoyl compound brombenzylmalonic nitrile is not affected by aqueous sodium hydroxide. Heated, it distils with decomposition, giving off hydrobromic acid. The distillate is a solid which melts at 70° when recrystallized from alcohol; this is probably a mixture of unchanged substance and benzalmalonic nitrile, whose melting-point is given by Heuck[1] as 87°. Treatment with alcoholic potash converted brombenzylmalonic nitrile, into a dark, thick oil, which refused to solidify, and was not further examined.

Carbethoxybenzylmalonic Nitrile (*Benzyldicyanacetic Ether*),



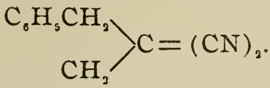
$\left.\begin{matrix}C_6H_5CH_2\\C_2H_5OOC\end{matrix}\right\rangle C{=}(CN)_2$.—Four grams of sodium benzylmalonic nitrile were added to an absolute ethereal solution of 2.48 grams (1 molecule) of chlorcarbonic ether. Reaction set in at once, and was controlled by cooling the mixture with water. After twenty-four hours the sodium chloride produced was filtered off, the ether evaporated *in vacuo*, and the solid residue recrystallized from a mixture of absolute ether and ligroin (40°–60°). The yield was 3 grams, or 60 per cent of the theory. A nitrogen determination of the product gave the following result:

0.1655 gram substance gave 18.6 cc. N_2 at 20° and 740.8 mm.

	Calculated for $C_{13}H_{12}N_2O_2$.	Found.
N	12.28	12.58

Carbethoxybenzylmalonic nitrile is soluble to a slight extent in water and in ligroin (70°–80°), more soluble in ether, and very soluble in alcohol. It crystallizes in large, colorless prisms melting at 44°–45°. Caustic soda acts upon it slowly in the cold, but more readily when hot, evolving ammonia.

Methylbenzylmalonic Nitrile,



$\left.\begin{matrix}C_6H_5CH_2\\CH_3\end{matrix}\right\rangle C = (CN)_2$. — This substance was prepared from both the silver and the sodium salt of benzylmalonic nitrile.

a. 3.7 grams of silver benzylmalonic nitrile were added, in several portions, to 6 grams (3 molecules) of methyl iodide. The salt hissed like hot iron on coming in contact with the methyl iodide, and the latter was, therefore, diluted with 10 volumes of absolute ether. After the addition of all the silver salt the mixture was warmed to the boiling-point of the ether. The silver iodide formed was then filtered off and the ethereal solution was treated with caustic soda, dried with calcium chloride, and distilled. The ethereal distillate had a faint odor of isonitrile. The residual oil solidified, on cooling, to a colored, crystalline mass, which was obtained perfectly white by treatment, in ligroin solution, with animal charcoal. The yield of crude product was 2.2 grams, or 92 per cent of the theory. The substance was dried *in vacuo* and analyzed with the following results :

---

[1] Heuck: Ber. d. chem. Ges., **28**, 2253.

I. 0.0984 gram substance gave 0.2804 gram CO_2, and 0.0507 gram H_2O.

II. 0.0774 gram substance gave 11.5 cc. N_2 at 21°.5 C. and 747.7 mm.

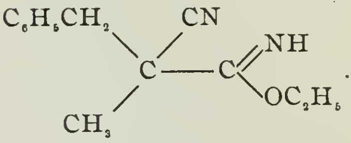
	Calculated for $C_{11}H_{10}N_2$.	Found.	
		I.	II.
C	77.65	77.70	....
H	5.88	5.73	....
N	16.47	....	16.68

Methylbenzylmalonic nitrile is readily soluble in ether and in alcohol, and slightly soluble in water and in ligroin. It crystallizes from water in needles and from ligroin (70°–80°) in large prisms, melting at 94°–95°.

b. Sodium benzylmalonic nitrile reacts only very slowly with methyl iodide. After several days' standing large, colorless, hexagonal plates separated from the mixture. These melted at 94°–95°, and had all the other properties of the substance made from the silver salt.

Action of Benzylmalonic Nitrile with Methyl Iodide and Alcoholic Sodium Ethylate.

Methylbenzylcyanacetimido Ethyl Ester,



$(C_6H_5CH_2)(CH_3)C(CN)—C(=NH)OC_2H_5$

.—3 grams of benzylmalonic nitrile, dissolved in absolute alcohol, were treated with an alcoholic solution of 0.45 gram (1 atom) of sodium and with 2.7 grams (1 molecule) of methyl iodide. There was an evolution of heat, and the mixture became neutral in twenty minutes. The alcohol was then distilled and the residue treated with water and extracted with ether. After treatment with caustic soda the ethereal solution was dried with chloride of calcium, and the ether evaporated. An almost colorless oil remained, which distilled at reduced pressure (170° at 22 mm.) without decomposition. The yield was 3.5 grams, or 85 per cent of the theory.

An analysis gave the following results:

I. 0.1750 gram substance gave 0.4624 gram CO_2, and 0.1198 gram H_2O.

II. 0.1555 gram substance gave 18.2 cc. N_2 at 21° and 742.6 mm.

	Calculated for $C_{13}H_{16}N_2O$.	Found. I.	II.
C	72.22	72.06	....
H	7.41	7.61	....
N	12.96	....	13.08

The product obtained in the case of the Conrad-Limpach reaction is, therefore, not the nitrile, but the imido ether.[1] This is a faintly aromatic, colorless oil, insoluble in water and in caustic soda. When its alcoholic solution is treated with concentrated hydrochloric acid a white precipitate of ammonium chloride is instantly formed. After standing six months the oil became so viscous that it could hardly be poured, yet all attempts to make it solidify were unsuccessful. The properties of the substance had also changed; ether dissolved it only partially, leaving a white, amorphous solid. That the imido ether obtained in the reaction described above is formed from the nitrile by the addition of alcohol is proved by the behavior of methylbenzylmalonic nitrile with sodium ethylate. Methylbenzylmalonic nitrile (1.2 grams) dissolved in absolute alcohol was treated with an alcoholic solution of 0.16 gram (1 atom) of sodium. No change was noticed, except that the solution became slightly colored. After standing at the ordinary temperature over night the mixture was poured into water and the separated oil extracted with ether. A substance was obtained which boiled at 156° at 9 mm.; weight, 1.15 grams, or 75 per cent of the theory.

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[1] Cf. Nef: Ann. Chem. (Liebig), **287**, 273, 315-8, 343. Also Hesse: This Journal, **18**, 744.

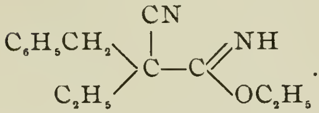
A nitrogen determination resulted as follows:

0.2066 gram substance gave 24.3 cc. N_2 at 21° and 746.8 mm.

	Calculated for $C_{13}H_{16}N_2O$.	Found.
N	12.96	13.22

This substance is identical in every respect with the imido ether described above.

Ethylbenzylcyanacetimido Ethyl Ester,



.—This compound was prepared from both ethyl and benzylmalonic nitrile.

a. 2 grams ethylmalonic nitrile, dissolved in absolute alcohol, were treated with an alcoholic solution of 0.5 gram (1 atom) of sodium and with 2.7 grams (1 molecule) of benzyl chloride. The temperature of the mixture rose to 50°. After the distillation of the alcohol, water was added to the residue and the separated oil extracted with ether, washed with sodium hydroxide, and dried with calcium chloride. Distillation of the ether left a product boiling at 170° at 22 mm.; weight, 3.5 grams, or 71 per cent of the theory.

A nitrogen determination gave the following result:

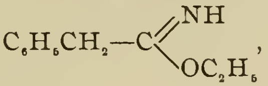
0.2339 gram substance gave 25.4 cc. N_2 at 19° and 744.5 mm.

	Calculated for $C_{14}H_{18}N_2O$.	Found.
N	12.18	12.28

This substance is decomposed by concentrated hydrochloric acid, like all imido ethers, with separation of ammonium chloride. It is colorless when freshly prepared, but becomes brown on standing.

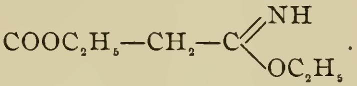
b. 1 gram benzylmalonic nitrile, dissolved in absolute alcohol, was treated with an alcoholic solution of 0.13 gram (1 atom) of sodium and with 2 grams (2 molecules) of ethyl iodide. A product (0.9 gram, *i. e.*, 75 per cent of the theory) boiling at 171° at 23 mm., and identical in its properties with the imido ether described under *a* was obtained.

Finally, there is appended here a description of a convenient method of preparing *phenylacetimido ether*,



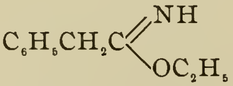
$$C_6H_5CH_2{-}C\left\langle\begin{array}{l}NH\\OC_2H_5\end{array}\right.,$$

and *monimidomalonic ether*,



$$COOC_2H_5{-}CH_2{-}C\left\langle\begin{array}{l}NH\\OC_2H_5\end{array}\right. .$$

These substances are of interest especially because analogous compounds have been assumed as intermediate products in the conversion of malonic nitrile and its monalkylated derivatives into salts. A study of them will, therefore, be continued in this laboratory. Their behavior toward metals, amines, sodium ethylate, and alkyl iodides deserves special investigation.

Phenylacetimido Ethyl Ester,[1]  $C_6H_5CH_2C\left\langle\begin{array}{l}NH\\OC_2H_5\end{array}\right.$. — The hydrochloride of this substance was made from benzyl cyanide by the method of Pinner, and was obtained at first as a colorless oil, which solidified with much difficulty. The salt is perfectly white and odorless and very soluble in water, which decomposes it into phenylacetic ether and ammonium chloride.

The free imido ether was prepared from the hydrochloride by the method of Bushong :[2] 10 grams of the salt were added to an excess of 10 per cent sodium hydroxide cooled to 7° C., and the separated oil was taken up at once with ether and dried with calcium chloride. Distillation of the ether left a colorless substance, boiling at 105°–106° at 10 mm. pressure. The yield was 6.9 grams, or 84 per cent of the theory.

A nitrogen determination gave the following result :

0.1538 gram substance gave 12 cc. N_2 at 23° C. and 752.6 mm.

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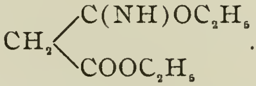
[1] Cf. Lückenbach : Ber. d. chem. Ges., **17**, 1421.

[2] This JOURNAL, **18**, 490.

	Calculated for $C_{10}H_{13}NO$.	Found.
N	8.59	8.75

The imido ether is insoluble in water and in aqueous alkalies. It distils at ordinary pressure with slight decomposition into alcohol and benzyl cyanide. Treated, in absolute ethereal solution, with metallic sodium, the imido ether gave a white, amorphous precipitate, which was not further examined.

Monimidomalonic Ether,[1] 

$$CH_2\left\langle\begin{array}{l}C(NH)OC_2H_5\\COOC_2H_5\end{array}\right.$$

.--The hydrochloride of this substance was made from cyanacetic ether by the method of Pinner. The salt was obtained as a colorless oil, which solidified, when shaken with cold ether, to a white, crystalline mass. It is soluble in cold water without decomposition, but on heating malonic ether is set free.

The free imido ether (made by adding the hydrochloride to cold 10 per cent sodium hydroxide) is a colorless oil, distilling at reduced pressure without decomposition. Heated at ordinary pressure, however, to 165°, it is decomposed into alcohol (75 per cent of the theoretical amount was obtained), and a thick, pasty mass, India-red in color, and insoluble in ether and in alcohol.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE PHENYLHYDRAZONES OF BENZOIN.

By Alexander Smith.

Some years ago,[2] in association with Mr. J. H. Ransom, I described the preparation and properties of a substance formed by the interaction of phenylhydrazine and benzoin which differed in physical properties, although not in chemical properties or composition, from the phenylhydrazone of Pickel.[3] The new compound, being more soluble, somewhat less stable, and of lower melting-point than the old one, was characterized as the β-form. In accordance with the view then (and now) prevailing in regard to such cases, the forms were held to be stereoisomers :

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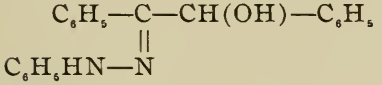
[1] Cf. Oppenheimer : Ber. d. chem. Ges., **28**, 478.

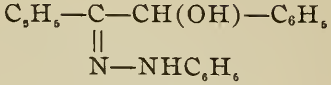
[2] This Journal, **16**, 108.

[3] Ann. Chem. (Liebig), **232**, 229.



$$\begin{array}{l} \quad C_6H_5—\overset{\displaystyle C}{}—CH(OH)—C_6H_5 \\ \qquad\quad \| \\ C_6H_6HN—N \end{array}$$

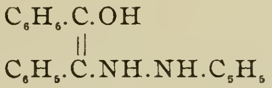
α-Phenylhydrazone, m. p. 158°–159°.



$$\begin{array}{l} C_5H_5—C—CH(OH)—C_6H_5 \\ \quad\;\;\; \| \\ \quad\;\;\, N—NHC_6H_6 \end{array}$$

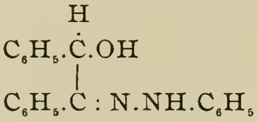
β-Phenylhydrazone, m. p. 106°.

The relation between these bodies has recently[1] been investigated by Freer. His results are, in several important particulars, in conflict with those of Smith and Ransom. He did not succeed in obtaining the substances in pure form by the methods indicated by Smith and Ransom, and explains the discrepancies between their results and his by the hypothesis that they used mixtures of the two isomers in their experiments. He reports that he was not able to convert the *β*- into the *α*-form by boiling with excess of phenylhydrazine in alcoholic solution. He also finds that the bodies behave differently towards benzoyl chloride and nitrous anhydride, founding on this the conclusion that they are not stereoisomers, but structurally different. The *β*-form he classes with the hydrazo-derivatives, the *α*-form with the hydrazones :



$$\begin{array}{l} C_6H_6.C.OH \\ \qquad\;\, \| \\ C_6H_5.C.NH.NH.C_5H_5 \end{array}$$

β-form.



$$\begin{array}{l} \qquad\quad\;\, H \\ C_6H_5.\dot{C}.OH \\ \qquad\quad\;\, | \\ C_6H_5.C : N.NH.C_6H_5 \end{array}$$

α-form

From the action of benzoyl chloride on the *β*-form he obtains a *γ*-phenylhydrazone (m. p. 162°) which he hesitates to class definitely as a stereoisomer of the *α*-body.

Being unable to account for these observations, I have reexamined the properties of the substances. I find that there is nothing to modify in the statements of Smith and Ransom called in question by Freer, that the supposed differences in the chemical behavior of the *α*- and *β*-forms are non-existent, and that the new *γ*-phenylhydrazone is not a phenylhydrazone at all.

Transformation of the β- into the α-Form.

This was accomplished by Smith and Ransom[2] by boiling the pure β-phenylhydrazone in alcoholic solution with two molecular proportions of phenylhydrazine for eighteen hours. A 50 per cent yield of the α-form was easily obtained. Freer states[1] that when he repeated this experiment with 2 grams of the "pure" β-phenylhydrazone, only 0.05 gram of the α-body was produced. Our result is explained by the naive assumption that we used a mixture of the β- and α-forms in all our work, and has simply recovered the latter. This hypothesis is inconsistent with Freer's own statement[2] that the product of the interaction of phenylhydrazine and benzoin, by the method used by us in preparing the β-body, contains 1 part of the α-body to 6 parts of the β-body. This would indicate that, even without purification, our β-substance could not have contained more than 15 per cent of the α-form. It is needless to say that the β-substance we used was always tested most rigidly as regards freedom from the α-form before use.

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[1] This JOURNAL, **21**, 22 and 45.

[2] *Ibid.*, 115.

Fortunately, there was still in my possession a portion of the β-phenylhydrazone originally used in this work, as well as a sample of the α-form made from it by transformation. Beyond a slight coloration, they had remained unaltered by keeping for five years. The β-body was found still to be perfectly pure. It dissolved instantly and completely in cold glacial acetic acid (the test for the absence of the α-modification given by Freer himself), and fulfilled also the more rigid tests of purity we had habitually applied. The α-body still melted at 158°–159°.

The transformation has now been repeated several times successfully by following the directions originally given by Smith and Ransom. The β-body used was perfectly homogeneous under the microscope, dissolved instantly in cold glacial acetic acid, and melted sharply at 106°. The phenylhydrazine (Kahlbaum's) was purified for use by freezing one-third of a large quantity, rejecting the unfrozen part, melting the crystals, and freezing one-third of the resulting liquid. The only difficulty encountered was that, in one case when a large flask connected with an upright condenser was used, a portion of the material was oxidized to the osazone of benzil, through the exposure of a larger surface than usual to the air. All danger from this source may be avoided by using a sealed tube. One experiment made in this way, with a shorter allowance of time than that formerly given, may be quoted.

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[1] This JOURNAL, 21, 49.

[2] *Ibid.*, 48, foot-note.

The β-phenylhydrazone (2 gr. = 1 mol.) and phenylhydrazine (1.4 gr. = 2 mol.) were dissolved in absolute alcohol (30 cc.) and heated at 100° for eight hours. The resulting pale-yellow liquid was concentrated on the water-bath and then left to evaporate spontaneously. The residue solidified almost completely to a mass of crystals which were freed from most of the adhering oil by pressing on a filter and spreading on a porous tile. This impure product weighed 1.5 grams. Even in this crude condition it softened at about 106°, but did not melt completely till a much higher temperature was reached. By agitation with cold glacial acetic acid for a few minutes the unchanged β-form, along with a small portion of the α-body, was removed. The undissolved material, when dry, weighed 0.65 gram and melted at 157°–158°. As an additional safeguard, 1 gram of the β-phenylhydrazone used in this experiment was agitated with the same proportion of cold glacial acetic acid for about the same time. It dissolved completely.

The γ-Phenylhydrazone of Freer.

By the action of benzoyl chloride on an ethereal solution of the β-phenylhydrazone, in the cold, Freer obtained a substance forming plates, with mother-of-pearl luster, melting at 162°. This, along with the hydrochloride of a base, whose nature was not determined, was deposited during the course of two days. The mother-liquor, on evaporation, was found to contain benzil and unchanged benzoyl chloride and tar.

This experiment was repeated and the substances described by Freer were obtained with ease. The hydrochloride of a base turned out to be largely ammonium chloride mixed with a little of the hydrochloride of a solid base which was not further examined. Freer's analysis and molecular weight determinations assign the formua $C_{20}H_{18}N_2O$ to the body melting at 162°. He regards it therefore as a new isomer and names it the γ-phenylhydrazone of benzoin. The α- and γ-forms he considers true phenylhydrazones and the β-body a hydrazo-derivative.

A brief examination of the substance sufficed to raise suspicion that it was not a phenylhydrazone at all. It distilled without decomposition. It could be boiled with benzaldehyde over the naked flame without interaction. It was heated in a sealed tube with concentrated hydrochloric acid for two hours at 100°, and a large part found to crystallize out of the hot acid in radiating needles, very unlike the ordinary plate form, having suffered, however, no chemical change. Now the α- and β-phenylhydrazones are decomposed by heat, react with benzaldehyde forming a substance[1] melting at 215°–216°, and turn to tar when left in contact with concentrated hydrochloric acid even in the cold.

At this point it was observed that the percentage of nitrogen given by Freer (9.42) was not in agreement with the data accompanying it (which gave 8.93, over 30 per cent caustic potash, 9.2 dry), and another estimation of the nitrogen was made. The percentage found was 7.2. This, with the combustion figures given by Freer, suggested $C_{13}H_{11}NO$ as a probable formula. The molecular weight of this body being much smaller than the values observed by Freer, two determinations of this constant were made in boiling alcohol by a modification of Walker and Lumsden's method[2] devised by Dr. McCoy. The following table shows the results of Freer's and my own measurements:

0.1667 gram substance gave 14 cc. nitrogen at 31° and 743 mm. (Freer).

0.2419 gram substance gave 15.8 cc. nitrogen (over 30 per cent KOH) at 24° and 743 mm. (Smith).

Molecular weight in solution in absolute alcohol (Smith).

	Substance. Gram.	Volume of solution. cc.	Rise.
I.	0.432	20.4	0.148°
II.	0.432	22.0	0.144°

[1] This JOURNAL, **16**, 114.

[2] J. Chem. Soc., **73**, 502. The description of Dr. McCoy's modified apparatus will be published shortly.

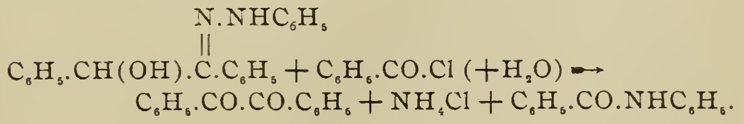
		Calculated for $C_{20}H_{18}N_2O$. γ-Phenylhydrazone.	Found. (Freer.)	Recalc. from Freer's data.	Calc. for $C_{13}H_{11}NO$.	Found. (Smith.)
C		79.43	79.13	....	79.19	....
H		5.96	6.09	....	5.58	....
N		9.27	9.42	8.93	7.11	7.20
Mol. wt.	I.	302.0	298.0		197.0	223.0
	II.		339.0			213.0

The composition, molecular weight, and melting-point being found to agree with those of benzanilide (m. p. 161°–162°), a little of the substance was mixed with a specimen of benzanilide, obtained from Kahlbaum, and the melting-point of the mixture was determined. No lowering in the melting-point, such as the introduction of a foreign substance would have caused, was observed, and the resolidified mixture, on being warmed once more, still melted sharply at 162°. To increase the certainty of this conclusion, a molecular-weight determination was made, with Kahlbaum's benzanilide, by McCoy's method:

	Substance. Gram.	Volume of solution. cc.	Rise.	Molecular weight found.
I.	0.626	15.2	0.299°	215
II	0.626	17.9	0.262°	208

A slight degree of association was to be anticipated in the case of benzanilide (mol. wt. 197) and was observed with both specimens to an equal extent, as the above results show.

This simple solution of the difficulty relieves us at once of the γ-form, and at the same time throws light on the formation of benzil and of the ammonia referred to above. The elements of water required for the change were not obtainable directly, since absolute ether was used as a solvent, and were probably taken from part of the benzoin. This would explain the formation of the considerable amount of tar mentioned by Freer and observed by me. The following equation represents the action in outline:



$$C_6H_5.CH(OH).\overset{\overset{\textstyle N.NHC_6H_5}{\|}}{C}.C_6H_5 + C_6H_6.CO.Cl\ (+H_2O) \longrightarrow$$
$$C_6H_6.CO.CO.C_6H_6 + NH_4Cl + C_6H_5.CO.NHC_6H_6.$$

β-Phenylhydrazone or Hydrazo Derivative?

According to Freer,[1] phenylhydrazine derivatives which can be oxidized to azo-bodies and react with benzoyl chloride forming either diacyl substitution-products, or " bodies from which dibenzoylphenylhydrazine can be obtained," are hydrazo compounds. On the other hand, " true hydrazones, which, of course, cannot be oxidized to bodies with the azo-structure, are either not acted on at all by acyl chlorides or they are converted into monoacylated derivatives or into monosubstituted phenylhydrazines." Freer's experimental results along these lines led him to classify the phenylhydrazones of acetone and acetophenone under the former head, and those of pyruvic ether and benzophenone under the latter.

Freer did not obtain any simple azo-compound, however, or, in the benzoyl chloride reaction, any other evidence that the β-phenylhydrazone of benzoin was similar to the hydrazides of acetone or acetophenone. Yet, in spite of this, he considers that "it is probably the hydrazo compound" (p. 53). The sole ground for this reasoning *per saltum* appears to be the bare fact that the α- and β-bodies behave differently in presence of benzoyl chloride and when treated with nitrous anhydride. With benzoyl chloride and the α-form no action at all was observed by Freer in the cold; the different behavior of the β-form is discussed above. With nitrous anhydride in dry ether, the β-form gave a red body of the nature of an addition-product with elimination of some water, while the α-form gave only a white substance bearing not even the remotest physical resemblance to the azo-compounds. These results, if confirmed by further work, might form a ground for believing that the substances are " structurally different," but surely not for deciding that the β-form is a hydrazo-compound.

I had no desire to take part in the task of determining the structures of hydrazones, and, in any case, should naturally avoid interfering with Freer's field of work. But my acquaintance with the properties of the two bodies in question made it difficult for me to believe that they would behave differently towards reagents like benzoyl chloride and nitrous anhydride. At the time of the discovery of the β-form, the hydrazo-structure seemed scarcely probable in view of its stability in air. The hydrazo-compounds, from acetone and acetophenone, both become red and finally tarry in a very short time. The β-body showed no such tendency. This conclusion is only strengthened by the fact, mentioned above, that a period of five years, even, has not affected its purity. The actions of benzoyl chloride and nitrous anhydride were therefore tried with the α-body. The details are given below. From the α-body exactly the same substances were obtained, in about the same quantity and proportions, as from the β-body. This can hardly be explained on the assumption that the products arose from admixture of some of the β-derivative. A specimen of the α-phenylhydrazone, melting sharply at 158°–159° (the m. p. of the pure body originally published by me and accepted by Freer) could not have contained such a proportion of the β-body (m. p. 106) as to give as good yields as the β-body itself. I can draw no other conclusions than that the products, formed from the β-body in the one case, came from the α-body in the other.

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[1] *Ibid.*, 19.

Action of Benzoyl Chloride on the α-Phenylhydrazone of Benzoin.

The exact proportions and conditions used by Freer (p. 45) for the β-body were observed. The α-body (3.5 grams) was dissolved in absolute ether and an equal amount of benzoyl chloride was added to the cold solution. The turbidity was somewhat longer in making its appearance than in the case of the β-body. But after 2–3 days the yellowish, crystalline substance deposited ceased to increase in quantity. The ethereal liquid was poured off, and the solid washed with a little pure ether, and then, to dissolve the hydrochloride, with water. The addition of sodium hydroxide to the aqueous extract liberated ammonia, which was distilled off and found, by titration, to be equivalent to 0.11 gram of ammonia. A small amount of a solid base also separated. The remainder of the solid body was recrystallized from alcohol and found to melt at 162° and be identical in physical properties with the benzanilide formed from the β-phenylhydrazone. A further quantity of the same substance was isolated from the mother-liquor after evaporation. The total amount obtained from 3.5 grams of the hydrazone was 1.3 grams. The mother-liquor gave also unchanged benzoyl chloride, benzil (1 gram) and uncrystallized tar. From 5 grams of the β-body Freer obtained 2.7 grams of the "γ-phenylhydrazone" (benzanilide) and 1.7 gram of benzil, so that the proportions for the α-body are approximately the same. This reaction gives, therefore, no ground for inferring any difference in structure in the two forms of the phenylhydrazone.

Action of Nitrous Anhydride on the Phenylhydrazones.

In Freer's experiment the β-phenylhydrazone was dissolved in absolute ether and cooled by a freezing-mixture. He allowed nitrous anhydride to pass in slowly until a transitory red tint gave place to a green color. The solution was then agitated with potassium carbonate solution. A red crystalline substance soon appeared in the ether which, when purified, melted at 137° with decomposition. Freer assigns to this substance the formula $C_{20}H_{16}N_6O_6$.

On treating the α-body in the same way, Freer obtained a dense, white crystalline precipitate, which converted the ethereal solution into a thick paste. The nature of this substance was not determined. He adds, "I was unable to obtain any of the red body derived from the β-hydrazone, on using the *pure* α-body, but I did observe its formation when using a sample prepared according to Smith and Ransom's directions. This result was probably due to the fact that some of the β-variety was present in the latter instance." The italics are Freer's.

The writer has been more fortunate, as from 5 grams of the *pure* α-body, purified according to Freer's directions, he had no difficulty in obtaining 1.8 grams of the same red substance in the first crop of crystals. The mother-liquor was not examined. Freer got 3.3 grams in all. After recrystallization from boiling benzene (solubility 1 in 20), the substance melted at 138° with decomposition. It was identical with the product from the β-body (first crop of crystals equals 1.2 gram), made for the purpose of comparison. In both cases a slight white precipitate made its appearance during the passage of the nitrous anhydride, but in neither case did the amount exceed a few milligrams.

These results show that either both phenylhydrazones of benzoin have the hydrazo-structure, or that, contrary to Freer's assumption, the formation of red bodies of this nature with nitrous anhydride may take place with true hydrazones. In the latter case, no ground for assigning a hydrazo-structure to either of the phenylhydrazones of benzoin would have survived closer examination.

To settle this point, the phenylhydrazone of benzophenone, a substance which Freer regards as undoubtedly a true phenylhydrazone, was subjected to the action of nitrous anhydride under conditions exactly the same as those described above. No white precipitate was observed. The ethereal solution deposited the expected red body (0.8 gram from 1 gram of the substance). It was very difficultly soluble and, when recrystallized from xylene, melted at 231°.

To avoid trespassing on Freer's territory the work was broken off at this point. For my purpose, it was sufficient to have shown that my former observations were correct, and that a consideration of all the facts leaves nothing which is inconsistent with the conclusion that the two phenylhydrazones of benzoin are stereoisomers.

In conclusion, I wish to express my thanks to Dr. H. N. McCoy for making the analysis and molecular weight determinations, as well as for assisting in the work described in the last section.

CHICAGO, June 7, 1899.

NOTES OF STUDENT WORK FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF VIRGINIA.

COMMUNICATED BY F. P. DUNNINGTON.

XXI.

168.—THERMAL EFFECTS OF THE DILUTION OF SOME SALTS.

BY F. P. DUNNINGTON AND T. HOGGARD.

It is well known that solutions of certain acids and salts when diluted with water occasion rise or fall of temperature. Much work upon this subject has been conducted by Regnault, Favre, Thomsen[1] and others and more recently by Prof. S. U. Pickering in his elaborate study on the nature of solutions. G. Lemoine has studied solutions of lithium chloride.[2] This work upon solutions of salts appears to have been confined chiefly to the determination of the thermal changes upon promptly dissolving salts in a large amount (100—1000 molecules) of water, which of course gives only the algebraic sum of all the changes of liquefaction, solution, and dilution. It therefore appeared desirable to examine a number of dissolved salts after the same manner as has been employed with the acids[3] to ascertain what classification, if any, they may show in this respect. Each salt was dissolved in the least integral number of molecules of water in which it could be readily dissolved at ordinary temperatures, 20°–25° C., and then, as each successive molecule of water was added to the strong solution, the calories evolved or taken up (+ or —) were estimated; a calorie being taken as the heat required to change one gram of water one degree centigrade in temperature. It is to be noted that the solutions used were not actually saturated, but had enough additional water to amount to a whole number of molecules before the measurements were begun, so that the change was not measured up to the point at which it is at a maximum.

The observations were made in thin beakers (in most cases) protected by cotton wool, using a mercury thermometer which could be read to $\frac{1}{20}$ degree centigrade, and all temperatures kept within two or three degrees of that of the atmosphere. The water to be added was brought each time to the temperature of the solution, or estimation made for the temperature of each liquid. The thermal effect of the beaker and thermometer was ascertained by experiments with water, and allowance also made for the specific heat of the dissolved salts.[4] In most cases the amount of the salt taken was its molecular weight in grams as given in the table, and where otherwise, the results are calculated to this amount. The heat developed is expressed in calories obtained from the gram-molecule of each salt. For example: lithium chloride, 42.5 grams is dissolved in four molecules (*i. e.* 72 cc.) of water, and the addition of the fifth molecule (18 cc.) of water develops a gain of 678 calories, the sixth gives 422 calories, the ninth, 141; the tenth and eleventh, 172 ($\frac{172}{2} = 86$) and the twelfth, thirteenth, and fourteenth, 159 ($\frac{159}{3} = 53$). Thus it will be seen that the blanks at the top of the table indicate the water required to effect solution, and the blank spaces below are followed by a figure which gives the average for that molecule and the blanks preceding it.

---

[1] Handbuch. d. Physik., Dr. A. Winkelmann (1896), Vol. II. p. 636.

[2] Compt. rend., 1897, **125**, 603.

[3] Watts' Dictionary (1875), Vol. III, p. 109.

[4] Phys. Chem. Tabellen, pp. 333; Landolt and Börnstein.

The first half of the table gives the results for salts which give only a rise in temperature; the second half gives results showing a fall in temperature. Because no refined method of obtaining these figures was available, they can only be considered as approximate, yet they show very clearly that most of the thermal change developed upon dilution of strong solutions takes place upon the addition of the first few molecules of water. Notably is this the case with sodium bromide, calcium chloride, magnesium nitrate, and potassium chloride.

On the other hand calcium nitrate presents a prominent exception to the other salts examined, in that it first evolves heat and subsequently absorbs it. In this one instance the observations were continued down to the 55th molecule of water and it seems probable that the slight irregularities shown are due to errors in observations, such as may be present in the other determinations also.

The special salts selected were taken because, of those which dissolve in a comparatively small amount of water, they only were available. It is to be noted that the highly deliquescent salts are those which afford most heat at the early stage of diluting; beyond this, there does not appear any generalization of the salts which act similarly.

CALORIES OBTAINED UPON THE ADDITION OF EACH MOLECULE OF WATER TO THE DISSOLVED SALTS.

Molecules of water.	Ammonium acetate.	Lithium chloride.	Sodium bromide.	Magnesium nitrate.	Calcium chloride.	Magnesium chloride.	Strontium chloride.
	77	42.5	103	148	111	95	158
1							
2							
3							
4	119						
5	103	678					
6	95	422		76			
7		230		37			
8	60	183		33			
9		141					
10	52						
11		86					
12	44			7	508		
13			223		123	370	
14		53	79			268	
15					66		64
16	30			1		109	23
17							
18		29	6			81	43
19					21		
20	27						25
21							
22		1	3			24	
23							
24							23
25					1		
26						14	
27							
28							
29							
30			2			2	14

CALORIES (—) OBTAINED UPON THE ADDITION OF EACH MOLECULE OF WATER TO THE DISSOLVED SALTS.

Calcium nitrate. 164	Ditto + $30H_2O$.	Ammonium nitrate. 80	Sodium nitrate. 85	Ammoniumchloride. 53.5	Sodium chloride. 58.5	Potassium chloride. 74.6	Potassium bromide. 119	Potassium iodide. 166
		—290						
	—36	—205						
		—172						
								—160
		—122	—87					
+131								
+ 41	—30	— 97	—50		—11		—139	— 48
+ 21					—11		— 73	
+ 8		— 68		—75	—12		— 77	
— 5				—54	—10	—221		
— 22			—16	—51		— 33	— 21	
— 29	—20			—31	—14			
— 53		— 46				— 0	— 23	— 11
— 34				—20	— 8			
			— 9	—18				
— 39							— 13	
	— 15	— 28		—23		— 0		
— 47								
				—15	— 1		— 8	— 6
— 36		— 19	— 6	—11				
	— 6				— 2			
							— 0	
	— 21					— 0		
— 45			— 1					— 1

UNIVERSITY OF VIRGINIA,
May, 1899.

169. ANALYSIS OF EMERY FROM VIRGINIA.

BY W. W. MILLER, JR.

This mineral was received from the late James F. Slaughter, Esq., of Lynchburg. It occurs in a heavy ledge near Whittle's, on the line of the Southern Railroad, in Pittsylvania Co. It is a black crystalline mass; magnetic; polar; sp. gr. = 4.205; emits the characteristic odor of emery; hardness, on edges = 8; infusible; and affords no loss upon intense ignition.

It may be dissolved by fusion with sodium acid sulphate. A portion heated to 450° C. with sulphuric acid in a sealed tube afforded estimations of silica and ferrous oxide. The rest of the analysis was made with a solution obtained by the successive action of hydrofluoric acid and sulphuric acid, showing the following composition:

		Molec. ratio.
Alumina	56.74	55.63
Ferric oxide	15.50	9.69
Ferrous oxide	20.77	28.85
Silica	0.68	
Titanic oxide	1.86	
Soda	3.95	
	99.50	

Soda is found in many of the silicates associated with emery, but in smaller amount than will account for its occurrence here. The amount of ferrous oxide in excess of that required to form magnetite is apparently present as hercynite, $FeAl_2O_4$. Omitting the silica, titanic oxide, and soda, the remaining constituents correspond to a mixture of magnetite 22.48 per cent, hercynite 33.34 per cent, and corundum 37.16 per cent. A thin section reveals the presence of two minerals other than the magnetite.

It seems most probable that the soda replaces some ferrous oxide in forming hercynite so that the amount of alumina existing as corundum is even less than that stated above.

While the substance is very tough and hard, it has not sufficient erosive power to give it value as emery. The emery of Chester, Mass., is similar to this in appearance, but Dr. J. Lawrence Smith considered that in it the whole of the alumina occurs as corundum and the iron as magnetite and that no hercynite is present. Probably the latter difference between these specimens accounts for the difference in erosive power.

UNIV. OF VA., June, 1898.

170. PRESERVATION OF HÜBL'S REAGENT.

BY RANDOLPH BOLLING.

One of the most satisfactory tests for the identification of certain fatty oils is that of Baron Hübl, consisting of a determination of the amount of iodine absorbed by the oil.[1]

The solution of iodine employed is known to lose strength rapidly; it was therefore proposed to determine the amount of this change under varying conditions, hoping thereby to obtain some improvement upon this feature of the test.

A solution was made up according to the formula given, with iodine 25 grams, mercuric chloride 30 grams, and strong alcohol (91 per cent) 1 liter. Portions of this were kept under different conditions:

Portion A—1. In clear glass, $\frac{1}{3}$ to $\frac{1}{4}$ filled, loosely stoppered, repeatedly opened and exposed to daylight.
“ “ 2. In clear glass, filled, closely stoppered, exposed to daylight.
“ “ 3. In amber glass, filled, closely stoppered, kept in darkness.

Another solution, B, was similarly made, but using absolute alcohol, and divided thus:

Portion B—2. Filled, closely stoppered, exposed to daylight.
“ “ 3. Filled, closely stoppered, kept in darkness.

In making the tests, 5 cc. of the solution were properly diluted and titrated with a standard solution of sodium thiosulphate. These solutions were thus tested as indicated during the first week, and then weekly. The following table gives the amount of free iodine found in 5 cc. at each test.

---

[1] J. Soc. Chem. Ind., 3, 641.

Free Iodine Present in 5 cc.

	A1.	A2.	A3.	B2.	B3.
Iodine dissolved.	0.1250	0.1250	0.1250	0.1250	0.1250
After 3 hours	0.1137	....	....	0.1149	....
" 2 days	0.1106	....	....	0.1125	....
" 4 "	0.1006	....	....	0.1106	....
" 7 "	0.0992	0.0980	0.0980	0.1095[1]	0.1052
" 2 weeks	0.0835	0.0883	0.0956	0.1016	0.1041
" 3 "	0.0844	0.0835	0.0876	0 0978	0.0992
" 4 "	0.0823	0.0799	....	0.0932	0.0847
" 5 "	0.0774	0.0774	0.0811	0.0932[1]	0.0883
" 6 "	0.0750	0.0738	0.0786	0.0895	0.0932
" 7 "	0.0702	0.0690	0.0738	0.0859[1]	0.0907[1]
" 8 "	0.0641	0.0629[1]	0.0702	0.0811[1]	0.0835[1]

It appears, therefore, that the alteration of this solution is very rapid and is delayed to but a small extent by employing absolute alcohol or by excluding air and light. There is full reason for the precaution of redetermining the strength of the solution whenever it is employed.

UNIV. OF VA., June, 1898.

171. DEHYDRATION OF CRYSTALS OF SODIUM PHOSPHATE.

BY T. C. WHITLOCK AND C. E. BARFIELD.

There is little definiteness, and some discrepancy, in the statements made as to the expulsion of water from crystallized disodic-hydrogen phosphate. We are told[2] "These crystals at 30° to 40° C. gradually give off their water of crystallization, and when heated to redness give off their basic hydrogen." Also by Fresenius:[3] "The water of crystallization is expelled by heating at 100° to a constant weight, and that of constitution by ignition."

It was therefore proposed to ascertain more exactly the conditions under which we may expel the water of crystallization and of constitution. These results are reached from the work of several students in this laboratory, many determinations, showing the gradual loss of water as the temperature was raised, are not given.

The following were obtained by Messrs. Whitlock and Barfield :

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[1] Began a new bottle kept under similar conditions, but previously unopened.

[2] Watts' Dictionary (1871), Vol. IV, p. 580.

[3] Quant. Anal., Braunschweig, 1887, S 781.

By reason of the readiness with which these crystals effloresce, the extent of dehydration was checked by a final ignition.

If the salt is put immediately into the steam-bath the crystals will melt and then the dehydration may require twelve hours or more.

The salt was gently heated on top of the steam-bath for from five to ten minutes, then in the bath (96° C.) for fifteen minutes, and then the loss

In	3 hours	at	150° C.	was	60.25	per cent
“	1 hour	“	170° “	“	60.22	“
“	1 “	“	180° “	“	60.30	“
“	1 “	“	190° “	“	60.33	“
“	1 “	“	200° “	“	60.26	“
“	1 “	“	200° “	“	60.35	“

At lower temperatures it required much longer to attain the same loss. The salt contains 60.343 per cent of water of crystallization.

The water of constitution was determined by further heating the above dehydrated residues. Portions were exposed for one hour to gradually increasing temperatures; *viz.*, 180°, 190°, 200°, 210°, 215°, 220°, with no loss. These, when heated severally to 230°, 240°, 250°, gave a little loss. In order promptly to remove this water, “dehydrated residues” were heated and the loss

In	1 hour	at	270° C.	was	1.80	per cent
“	2 hours	“	270° “	“	2.47	“
“	1 hour	“	275° “	“	2.44	“
“	1 “	“	280° “	“	2.23	“
“	1 “	“	290° “	“	2.43	“
“	1 “	“	300° “	“	2.48	“

Hence we see that the water of crystallization may be removed below 220° and (after efflorescence) at 180° in one hour, and that the water of constitution begins to be lost at 230°, and may be removed in one hour at 300°, or more promptly by a low red heat.

UNIV. OF VA., June, 1897.

172. EXAMINATION OF A SANDSTONE FROM AUGUSTA COUNTY, VIRGINIA.

By W. W. Miller, Jr.

About one-half mile east of Basic City there passes a line of hills, which rise at the foot of the western slope of the Blue Ridge and consist of Lower Cambrian Quartzite. The track of the Chesapeake and Ohio Railroad passes by one of these hills, and material from it is largely used by this railroad for ballast. This hill is covered with a coating 40 feet or more in thickness of the same composition as the rest of the hill, but consisting of a mass of angular fragments, mostly 2 or 3 inches in dimensions and graduating to a dust. This shattering seems to be the work of frost. In seams between the fragments there is a small amount of clay mixed with finely divided silica, which also is seen under the microscope to be in angular fragments. The deposit is readily loosened with a pick, and is then loaded upon cars for ballast. When this material is sifted to three or four sizes, laid, and beaten down for a pathway, with the coarser lumps at the bottom and finer on top, it soon becomes firm and compact, and yet allows rain to soak through it promptly. The peculiar property which it possesses of thus becoming compact when dumped and left undisturbed for a short time, led to seeking an explanation of this fact through the following analyses of both the clay and the rock.

The fine powder was brought into solution by repeated fusion with sodium acid sulphate and treatment with hydrofluoric acid. The alkali was determined by Dr. J. Lawrence Smith's method. The following results were obtained :

	Clay.	Rock.
Alumina	24.23	2.37
Titanic oxide	0.94	0.00
Ferric oxide	3.57	0.46
Magnesia	1.25	0.00
Potash	4.04	0.00
Soda	0.77	0.19
Water, lost at 100° C.	0.49	0.00
" " by ignition	4.83	0.26
Silica, amorphous, free	0.53	0.00
" cryst. and combined	63.68	by diff. 96.72
	99.29	100.00

The clay was treated with hydrochloric acid, and the filtrate proved to contain no alkali. Hence it appears that the alkali is contained in form of a silicate. There are, moreover, geological reasons for stating that feldspar is being formed and silica altered to quartzite. As these results present no chemical explanation of the peculiar property, most probably it is due solely to physical causes. Being in sharp, angular pieces with rough fracture, these readily hold in place when once packed, the finer portion filling in the cavities. Moreover, this packing takes place most readily when compacted by use when the pathway is wet.

UNIV. OF VA., May, 1899.

173. SOLUBILITY OF LEAD SULPHATE IN AMMONIUM ACETATE.

BY J. C. LONG.

In the estimation of lead as sulphate, occasionally it is desirable to bring it into solution so as to separate and purify it for weighing. Among the solvents to be employed for this purpose, a solution of ammonium acetate is most recommended. The action of this solvent, though often mentioned, is not fully described, and the only figure given in Storer's "Dictionary of Solubilities" is that of Bolley, stating that "at 12.5° C. one part of lead sulphate is soluble in 47 parts of a solution of ammonium acetate having sp. gr. = 1.036" (= 18 per cent). Hence it appeared desirable to define more closely the conditions under which this operation is best conducted.

A preliminary test was made with portions of pure precipitated lead sulphate, which indicated that it required for its solution about 10 parts of a solution containing 56 grams of ammonium acetate in 100 cc. Then taking 0.5 gram of lead sulphate and 5 cc. of the above solution in each of several test-tubes, to these there was added of

Water:	0	1	2	3	4	5	6	7 cc. giving
Approx.:	56	46	40	35	31	28	25	23 grams in 100 cc.

With agitation, these were digested at 100° C., and it appeared that the solution of 35 "volume per cent" was the first to leave no residue.

An excess of lead sulphate was boiled with solutions of ammonium acetate of various strengths, digested at 100° C. and filtered through dry papers; 5 grams of the filtrate were taken in each case and found to afford the results given in the table.

In 100 cc. $NH_4C_2H_3O_2$.	$PbSO_4$ dissolved in grams.			5°.
	Hot.	Cooled.	Cooled, 24 hours.	
28	0.356	....	....	3.47
30	0.418	....	0.226	3.12
32	0.494	0.451	0.242	2.73
35	0.513	0.452	....	2.89
37	0.529	....	0.238	2.90
40	0.539	....	0.263	3.27
45	0.555	0.488	....	3.34

In column 5° there is given, for each of the several degrees of dilution, the weight of ammonium acetate required to dissolve 1 gram of lead sulphate, from which it is seen that when in a solution of from 31 to 37 "volume per cent" (29 to 34.3 per cent) the ammonium acetate has the greatest solvent power.

In order, therefore, to dissolve lead sulphate, for each gram add 10 cc. of a 33 per cent. solution of ammonium acetate (sp. gr. = 1.07), heat to boiling, and filter promptly. In recovering the lead sulphate, it was found that the addition of 0.5 gram sulphuric acid greatly facilitated the evaporation and expulsion of the ammonium acetate, without loss.

UNIV. OF VA., June, 1898.

174. ANALYSIS OF SMITHSONITE FROM ARKANSAS.

BY W. W. MILLER, JR.

This mineral was received from the "Morning Star" Mine, in Searcy Co., on a branch of the White River, about 50 miles above Batesville, Ark. It occurs in a botryoidal form, enclosing zinc blende in layers 6 to 8 mm. thick, and encrusted by a thin layer of amorphous smithsonite. It is grayish-white in color, luster pearly, translucent, hardness = 5, sp. gr. = 4.179.

Upon analysis it afforded the following:

Zinc oxide	63.67
Cadmium oxide	1.06
Cupric oxide	0.21
Ferrous oxide	0.07
Carbon dioxide	34.69
Silica	0.52
	100.22

It proves, therefore, to be a pure variety of smithsonite, in which a little cadmium, copper, and iron replace zinc.

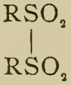
UNIV. OF VA., June, 1898.

DISULPHONES AND KETOSULPHONES.

BY ELMER P. KOHLER AND MARGARET B. MACDONALD.

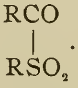
The investigations of Otto and of Baumann have led to the discovery of excellent methods for the preparation of all classes of sulphones except disulphones and ketosulphones of the types represented by the formulas:

I.



$$\begin{array}{c}RSO_2\\|\\RSO_2\end{array}$$

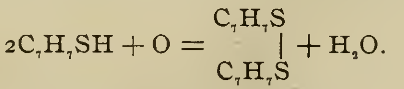
II.



$$\begin{array}{c}RCO\\|\\RSO_2\end{array}.$$

It seemed of particular interest to prepare members of the first class, because no substances are known that contain two hexavalent sulphur atoms in direct union. The marked tendency of sulphur to combine with sulphur, that is observed in the case of sulphides and other compounds containing bivalent sulphur, is absent in compounds containing hexavalent sulphur, and when sulphur compounds containing two sulphur atoms in direct union are oxidized, the union between the two is broken before both of them become hexavalent. These relations are illustrated by the following reactions:

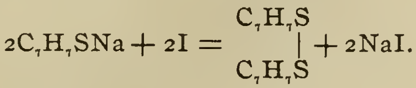
I.



$$2C_7H_7SH + O = \begin{array}{c}C_7H_7S\\|\\C_7H_7S\end{array} + H_2O.$$

$$C_7H_7SO_2H + O = C_7H_7SO_3H.$$

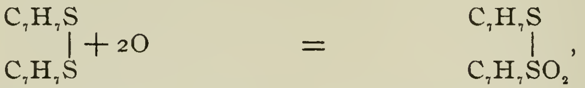
II.



$$2C_7H_7SNa + 2I = \begin{array}{c}C_7H_7S\\|\\C_7H_7S\end{array} + 2NaI.$$

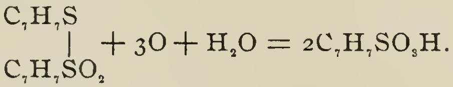
$$C_7H_7SO_2Na + I_2 = C_7H_7SO_2I + NaI.$$

By starting with disulphides, with two sulphur atoms in combination, it is possible to oxidize one to the hexavalent condition:



$$\begin{array}{c}C_7H_7S\\ |\\ C_7H_7S\end{array} + 2O = \begin{array}{c}C_7H_7S\\ |\\ C_7H_7SO_2\end{array},$$

but further oxidation breaks the union between the sulphur atoms and leads to sulphonic acids:

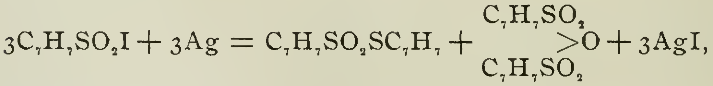


$$\begin{array}{c}C_7H_7S\\ |\\ C_7H_7SO_2\end{array} + 3O + H_2O = 2C_7H_7SO_3H.$$

Some time ago Otto[1] tried to prepare disulphones of the type I, by using the reactions that are constantly employed for linking two residues through carbon, but without success. Thus benzenesulphone chloride and sodium give only sulphinate:

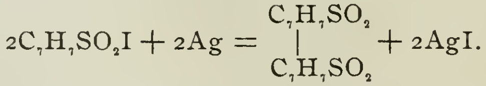
$$C_6H_5SO_2Cl + 2Na = C_6H_5SO_2Na + NaCl.$$

The sulphone iodides, which lose iodine with the greatest ease, give complicated reactions when heated with finely-divided silver:



$$3C_7H_7SO_2I + 3Ag = C_7H_7SO_2SC_7H_7 + \begin{array}{c}C_7H_7SO_2\\ \\ C_7H_7SO_2\end{array}\!\!>O + 3AgI,$$

instead of the simple reaction expected:



$$2C_7H_7SO_2I + 2Ag = \begin{array}{c}C_7H_7SO_2\\ |\\ C_7H_7SO_2\end{array} + 2AgI.$$

Because of these and similar reactions Otto[2] concluded that disulphones of type I were probably incapable of existence.

Some observations made in the course of an investigation of the reaction between metallic derivatives and sulphone chlorides led us to attempt the preparation of this class of substances in a different way. Among the reaction-products of perfectly pure aliphatic and aromatic sulphone chlorides with a variety of reagents, we have frequently observed a minute quantity of some sulphur compound, that, owing to its insolubility in water, generally forms a scum on the surface of the liquid used. The insolubility of the substance, its stability on heating, and its inertness to reagents, pointed to some kind of sulphone, while the fact that the same substance or similar substances are obtained in a great variety of reactions indicated that only the sulphone chloride is involved in its formation. In the investigation above referred to we noticed that a substance of this kind was formed only in those experiments in which there was protracted heating and an insufficient amount of base. This suggested that the substance might be a disulphone formed by the interaction of a sulphone chloride and a sulphinate :

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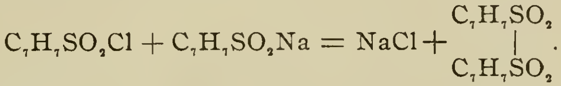
[1] Ber. d. chem. Ges., **24**, 478.

[2] *Loc. cit.*, **24**, 484.

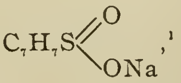


$$C_7H_7SO_2Cl + C_7H_7SO_2Na = NaCl + \begin{array}{c} C_7H_7SO_2 \\ | \\ C_7H_7SO_2 \end{array}.$$

We have found that this reaction gives a simple and, apparently, a perfectly general method for the preparation of disulphones of this kind.

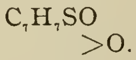
The reaction leaves but little doubt as to the structure of the substances obtained. If the sulphinate has the structure usually assigned to it and acts accordingly, the resulting substance must be a disulphone with the structure given. If, on the other hand, the sulphinate reacts in the desmotropic form :

I.



$$C_7H_7S\begin{array}{l} /\!\!/O \\ \backslash ONa \end{array},^{1}$$

the product might be an anhydride with the structure



$$\begin{array}{l} C_7H_7SO \\ \qquad\quad >O. \\ C_7H_7SO_2 \end{array}$$

This formula, however, is not at all in accord with the extreme stability of the substance. It is not changed by prolonged boiling with dilute or concentrated hydrochloric acid, and it can be crystallized, without loss, from concentrated nitric acid.

The success with the sulphone chlorides naturally sug-

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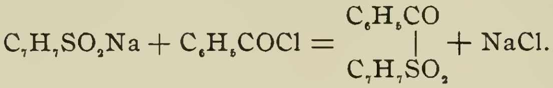
[1] Ber. d. chem. Ges., 18, 2493.

gested a similar experiment with other kinds of acid chlorides. We have found that the reaction works equally well for the preparation of ketosulphones :



$$C_7H_7SO_2Na + C_6H_5COCl = \begin{array}{c} C_6H_5CO \\ | \\ C_7H_7SO_2 \end{array} + NaCl.$$

The ketosulphones are remarkably active substances, giving all the typical ketone reactions, but showing a much more reactive oxygen atom than that in other ketones.

The two classes of substances are now under investigation, hence this paper is confined to those results which are necessary to show the general character of the reactions and the structure of the products.

Diparatolyldisulphone, $(p)CH_3.C_6H_4.SO_2.SO_2.C_6H_4.CH_3(p)$. —Paratoluenesulphone chloride and sodium paratoluenesulphinate react slowly in water, ether, benzene, and acetone. As the result of a number of experiments we have adopted the following method of procedure : 1 molecule of the sulphinate is placed in a flask with sufficient water to form a thick paste; 1 molecule of sulphone chloride and a small quantity of ether are added to this, and the whole warmed in a water-bath until all of the sulphone chloride has disappeared; or until the solid that separates no longer increases in amount. The liquid is then filtered while hot. The aqueous solution contains sodium chloride, sodium sulphonate, and sulphinic acid. It is neutralized with sodium carbonate, returned to the flask with another molecule of sulphone chloride and a small quantity of ether, and heated as before. The finely-divided crystalline solid obtained in the two operations, is boiled with water to remove small quantities of adherent sulphinic acid, dried on the water-bath, extracted with small quantities of boiling ether to remove any sulphone chloride carried down with it, and recrystallized from large quantities of benzene. From the concentrated solution in boiling benzene the substance separates, on cooling, in small, lustrous plates that adhere to the sides of the vessel. From a cold benzene solution it separates, on evaporation, in thick, monoclinic tables that sometimes reach a diameter of 5 to 6 mm. An analysis of the substance prepared in this way gave the following results :

I. 0.1551 gram substance gave 0.3073 gram CO_2, and 0.0597 gram H_2O.

II. 0.1609 gram substance gave 0.3196 gram CO_2, and 0.0621 gram H_2O.

III. 0.1273 gram substance gave 0.2041 gram $BaSO_4$.

IV. 0.1960 gram substance gave 0.2919 gram $BaSO_4$.

V. 0.1503 gram substance gave 0.2259 gram $BaSO_4$.

	Calculated for $C_7H_7SO_2$.	Found.				
		I.	II.	III.	IV.	V.
C	54.19	53.9	54.1	....	....	....
H	4.51	4.26	4.3	....	....	....
S	20.64	...	...	20.49	20.45	20.64

A molecular weight determination by the cryoscopic method with naphthalene as the solvent gave the following results :

I. 1.63 grams substance per 100 grams of solvent gave a mean depression of 0.355°.

II. 2.53 grams substance per 100 grams of solvent gave a mean depression of 0.565°.

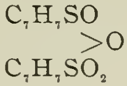
III. Constant for naphthalene 70.

	Calculated for $(C_7H_7SO_2)_2$.	Found.	
		I.	II.
Molec. wt.	310.0	321.0	313.0

The substance is insoluble in water and alcohol, very slightly soluble in ether, moderately soluble in chloroform and boiling benzene. In a capillary tube it melts with decomposition at about 212°. The substance is remarkably inert. It is not attacked by dilute acids or alkalies. When boiled with concentrated potash, however, it is slowly decomposed. The solution contains a sulphinate and a sulphonate, which were identified as follows : The clear solution in caustic potash was acidified with hydrochloric acid and extracted with ether. The ether, on evaporation, deposited crystals of paratoluenesulphinic acid melting at 85°. The aqueous solution from which all the sulphinic acid had been extracted was neutralized, evaporated to dryness, and extracted with absolute alcohol. The alcoholic extract was evaporated to dryness and treated with phosphorus pentachloride. It gave paratoluenesulphone chloride melting at 69°. The decomposition with alkalies, therefore, takes place according to the equation :

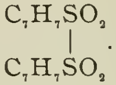
$$C_{14}H_{14}S_2O_4 + 2KOH = C_7H_7SO_2K + C_7H_7SO_3K + H_2O.$$

This reaction excludes all possible formulas except the two given in the introduction :

I. 

$$\left.\begin{matrix}C_7H_7SO\\C_7H_7SO_2\end{matrix}\right>O$$

and

II. 

$$\begin{matrix}C_7H_7SO_2\\|\\C_7H_7SO_2\end{matrix}.$$

A substance with the anhydride formula represented by I. ought to be as easily hydrolyzed by acids as by alkalies, but the substance in question can be boiled with concentrated or dilute hydrochloric acid without any appreciable change. It is, therefore, diparatolyldisulphone.

Phenylparatolyldisulphone, $C_6H_5.SO_2.SO_2.C_6H_4CH_3(p)$.—This substance was prepared from benzenesulphone chloride and sodium paratoluenesulphinate, and also from paratoluenesulphonechloride and sodium benzenesulphinate :

$$C_7H_7.SO_2Na + C_6H_5.SO_2Cl = C_7H_7SO_2.SO_2C_6H_5 + NaCl;$$
$$C_7H_7.SO_2Cl + C_6H_5.SO_2Na = C_7H_7SO_2.SO_2C_6H_5 + NaCl.$$

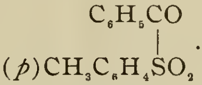
It closely resembles diparatolylsulphone in crystal form and properties. It is moderately soluble in ether and benzene, readily soluble in chloroform, and melts at 166°. When heated with caustic potash it gives potassium chloride, potassium benzenesulphonate, potassium benzenesulphinate, potassium toluenesulphinate, and potassium toluenesulphonate.

Paratolylparanitroorthotolyldisulphone $(4)CH_3.C_6H_4.SO_2.SO_2.C_6H_3.CH_3.NO_2(2,4)$.—This substance crystallizes from chloroform in large, thick prisms, melting at 154°. It is noteworthy that when paranitroorthotoluenesulphone chloride and sodium paratoluenesulphinate react in the presence of water, some diparatolyldisulphone is always formed, indicating that some of the chloride reacts with the sulphinate according to the equation :

$$C_7H_6NO_2SO_2Cl + C_7H_7SO_2Na = C_7H_6.NO_2.SO_2.Na + C_7H_7.SO_2Cl.$$

We have observed a reaction like this when sulphuryl chloride reacts with sulphinates in the presence of water:

$$C_7H_7SO_2Na + SO_2Cl_2 = C_7H_7SO_2Cl + NaSO_2Cl \longrightarrow NaCl + SO_2.$$

Phenylparatolylketosulphone,  $\begin{array}{c} C_6H_5CO \\ | \\ (p)CH_3C_6H_4SO_2 \end{array}$.—The sulphinates react with the chlorides of carbonic acids under the same conditions as those under which they react with sulphone chlorides. The best results are obtained by heating the sulphinates with ethereal solutions of the chlorides in sealed tubes.

Fifteen grams of benzoyl chloride, 20 grams of sodium paratoluenesulphinate, and 25 cc. of ether were heated to 110° for seventy-two hours. There was no pressure in the tube on opening. The contents were washed with water, and a solution of sodium carbonate added to remove sodium salts and unused benzoyl chloride. The aqueous solution contained sodium chloride, sodium sulphinate, and sodium benzoate, but no carbonate, sulphonate, nor sulphate. The ethereal solution was dried over anhydrous sodium sulphate, and the ether allowed to evaporate. There remained a clear, colorless oil, which could not be distilled without decomposition, and did not solidify on standing. This made it probable that the liquid obtained as a direct product of the reaction is the sulphoneketone expected, and that its solidification in contact with sodium carbonate is due to the addition of water. This was confirmed by the behavior of the liquid with water and alcohol. If it is digested with water on a water-bath for from ten to fifteen minutes, and then allowed to cool, it solidifies completely, the solid melting at 80°. If it is boiled with a small quantity of absolute alcohol for a short time, the corresponding crystalline alcoholate is obtained.

The substance is exceedingly stable; it does not lose water below 150°, and it is not possible to drive off all of the water without decomposing the substance. Both the oil and the solid readily react with the ordinary reagents for ketones, the oil being much more reactive than the solid. If the oil is shaken with a concentrated solution of hydrogen potassium sulphite it rapidly goes into solution, but in a short time a beautiful crystalline addition-product begins to separate. The solid does not dissolve in hydrogen potassium sulphite. When allowed to stand in contact with a cold solution of sodium carbonate for several days the oil solidified to a white, crystalline mass. This was easily purified by recrystallization from low-boiling petroleum ether. It was thus obtained in thick needles melting at 80°.

I. 0.2755 gram substance gave 0.6130 gram CO_2, and 0.1480 gram H_2O.

II. 0.2077 gram substance gave 0.4608 gram CO_2, and 0.1007 gram H_2O.

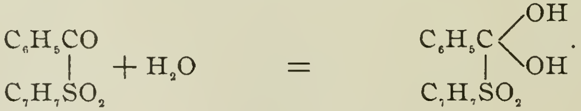
III. 0.1655 gram substance (crystallized from ether) gave 0.3680 gram CO_2, and 0.0720 gram H_2O.

IV. 0.2112 gram substance gave 0.1786 gram $BaSO_4$.

V. 0.1705 gram substance gave 0.1429 gram $BaSO_4$.

	Calculated for			Found.		
	$C_{14}H_{14}SO_4$.	I.	II.	III.	IV.	V.
C	60.5	60.7	60.5	60.6	....	....
H	5.04	5.3	5.2	4.8	....	....
S	11.51	...	...	...	11.6	11.45

The analyses show that the substance is not the ketosulphone looked for, but an exceedingly stable hydrate analogous to chloral hydrate :



$$\begin{array}{l} C_6H_5CO \\ \quad | \\ C_7H_7SO_2 \end{array} + H_2O = \begin{array}{l} C_6H_5C\begin{array}{l} \diagup OH \\ \diagdown OH \end{array} \\ \quad | \\ C_7H_7SO_2 \end{array}.$$

It gives the same product if allowed to remain in contact with the solution for several days. Both oil and solid readily combine with nascent hydrocyanic acid, and give crystalline condensation-products with hydroxylamine, phenylhydrazine, primary amines, and phenols.

The reaction by which the substance was prepared seems to be a general one, as we have found that it works equally well with acetyl chloride, succinyl chloride, cinnamyl chloride, and phthalyl chloride. This has made it possible to prepare and study ketosulphones of which no carbon analogues are known. We hope to be able to report on some of these in the near future.

BRYN MAWR COLLEGE,
June, 1899.

THE REACTION BETWEEN SULPHONE CHLORIDES AND METALLIC DERIVATIVES OF KETONIC ESTERS.

By Elmer P. Kohler and Margaret B. MacDonald.

The reaction between acid chlorides and the metallic derivatives of ketonic esters and polyketones has been studied with great care, but the investigations have been confined to the chlorides of carbonic acids. In the cases studied the general result has been the replacement of one or more atoms of the metal by a corresponding number of acidyl groups. It is known, however, that the reaction between sulphone chlorides and metallic derivatives in general, is not nearly so uniform as that between other acid chlorides and the same substances. With alcoholates and phenolates the sulphone chlorides react like other acid chlorides, forming esters by double decomposition. With mercaptides a reaction similar to this takes place, but it is accompanied by a second one resulting in the formation of a sulphinate and a disulphide:

$$\text{I.}\quad C_7H_7SO_2Cl + NaSC_5H_{11} = C_7H_7SO_2SC_5H_{11} + NaCl\ ;^1$$

$$\text{II.}\quad C_7H_7SO_2Cl + 2NaSC_5H_{11} = C_7H_7SO_2Na + (C_5H_{11}S)_2.$$

With sulphides, thiophenolates, and zinc alkyls, only reactions of the second type have been observed:

$$\text{I.}\quad C_7H_7SO_2Cl + K_2S = C_7H_7SO_2K + KCl + S\ ;^2$$

$$\text{II.}\quad C_7H_7SO_2Cl + 2NaSC_6H_5 = C_7H_7SO_2Na + (C_6H_5S)_2\ ;^3$$

$$\text{III.}\quad 2C_6H_5SO_2Cl + Zn(C_2H_5)_2 = (C_6H_5SO_2)_2Zn + 2C_2H_5Cl.^4$$

In nearly all of these cases the sulphone chlorides seem to behave differently from other acid chlorides. It is possible, however, that in these cases the sulphinates are secondary products, formed because the chloride was added to an excess of the other reagent.

The preliminary experiments with paratoluenesulphone chloride and sodium acetoacetic ester showed that it is impos-

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[1] Blomstrand: Ber. d. chem. Ges., **3**, 963.

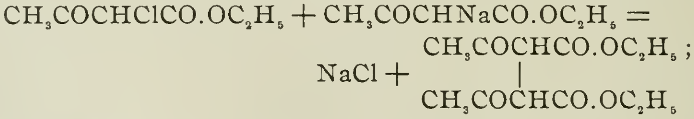
[2] Spring: Ber. d. chem. Ges., **7**, 1158.

[3] Otto: *Ibid.*, **15**, 128.

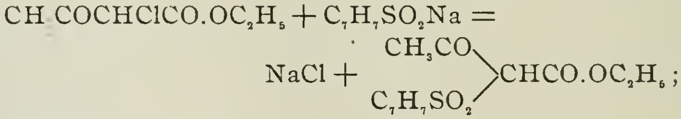
[4] Kalle: Ann. Chem. (Liebig), **119**, 156.

sible to get a complete reaction by using 1 molecule of the sodium derivative for 1 molecule of the sulphone chloride. If the relative amount of the former is increased until the mixture remains faintly alkaline after all of the sulphone chloride has disappeared, the main products are sodium chloride, sodium toluenesulphinate, and diacetosuccinic ester; but, in addition to these, acetoacetic ester, chloracetoacetic ester, and paratoluenesulphonacetoacetic ester are always formed. Similar experiments with sodium malonic ester and sodium acetylacetone gave analogous products. These substances, therefore, represent the normal products of the reaction between sulphone chlorides and the metallic derivatives of esters and ketones. All of them can easily be accounted for by assuming that the primary reaction is analogous to that which takes place between sulphone chlorides and zinc alkyls. In the case of acetoacetic ester this would lead to the following equations:

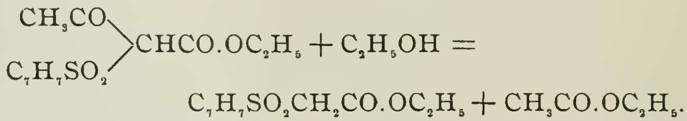
I. $C_7H_7SO_2Cl + CH_3COCHNaCO.OC_2H_5 = C_7H_7SO_2Na + CH_3COCHClCO.OC_2H_5$;

II. 

$$CH_3COCHClCO.OC_2H_5 + CH_3COCHNaCO.OC_2H_5 = NaCl + \begin{array}{l} CH_3COCHCO.OC_2H_5; \\ \qquad\quad | \\ CH_3COCHCO.OC_2H_5 \end{array}$$

III. 

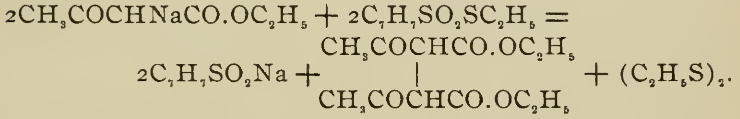
$$CH\ COCHClCO.OC_2H_5 + C_7H_7SO_2Na = NaCl + \left.\begin{array}{r} CH_3CO \\ C_7H_7SO_2 \end{array}\right> CHCO.OC_2H_5;$$

IV. 

$$\left.\begin{array}{r} CH_3CO \\ C_7H_7SO_2 \end{array}\right> CHCO.OC_2H_5 + C_2H_5OH = C_7H_7SO_2CH_2CO.OC_2H_5 + CH_3CO.OC_2H_5.$$

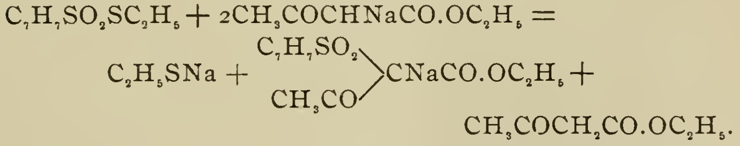
The third equation assumes the intermediate formation of a substance which was not isolated. All efforts to prepare this by the action of sodium sulphinate on chloracetoacetic ester failed; only the decomposition-products, ethyl acetate, and toluenesulphonacetic acid, were obtained. Attempts to condense acetoacetic ester and the sulphone chloride with potassium carbonate gave no better results, as the unused carbonate decomposes the condensation-product as fast as formed.

The sodium derivative of the substance was, however, finally obtained in small quantity by a reaction that has not hitherto been used for the preparation of this class of substances. It has been found[1] that sodium acetoacetic ester reacts with sulphocyanates to form a mercaptide and sodium cyanacetoacetic ester. It seemed possible that by substituting an ester of a thiosulphonic acid a similar reaction might be obtained, resulting in the formation of a mercaptide and the sulphonacetoacetic ester. It was found that sodium acetoacetic ester readily reacts with the ester of paratoluenethiosulphonic acid, in the cold. The principal reaction is represented by the equation :



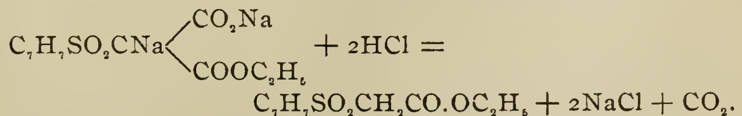
$$\mathrm{2CH_3COCHNaCO.OC_2H_5 + 2C_7H_7SO_2SC_2H_5 = 2C_7H_7SO_2Na + \begin{matrix}CH_3COCHCO.OC_2H_5\\ |\\ CH_3COCHCO.OC_2H_5\end{matrix} + (C_2H_5S)_2.}$$

A subordinate reaction gives sodium toluenesulphonacetoacetic ester according to the equation,



$$\mathrm{C_7H_7SO_2SC_2H_5 + 2CH_3COCHNaCO.OC_2H_5 = C_2H_5SNa + \begin{matrix}C_7H_7SO_2\\ CH_3CO\end{matrix}\!\!>\!CNaCO.OC_2H_5 + CH_3COCH_2CO.OC_2H_5.}$$

The sodium derivative thus obtained is extremely unstable, breaking down into sodium sulphonacetic ester and acetic acid with the greatest ease. The free ester seems incapable of existence. A similar difference in stability was observed in the case of malonic ester. One of the products of the reaction between toluenesulphone chloride and disodium malonic ester was an ester salt of sodium toluenesulphonmalonic acid. This was sufficiently stable to permit of recrystallization from boiling alcohol, but on acidifying it immediately decomposed into carbon dioxide and toluenesulphonacetic ester :



$$\mathrm{C_7H_7SO_2CNa\!<\!\begin{matrix}CO_2Na\\ COOC_2H_5\end{matrix} + 2HCl = C_7H_7SO_2CH_2CO.OC_2H_5 + 2NaCl + CO_2.}$$

[1] Kohler : This Journal, 22, 67.

Sodium Acetoacetic Ester and Paratoluenesulphone Chloride.

One gram-molecule of pure dry sodium acetoacetic ester and 1 gram-molecule of the sulphone chloride were brought together in absolute ether, and the mixture digested in a water-bath. After heating for an hour, a small portion of the mixture was removed and shaken with water. The aqueous solution was neutral to litmus, showing that all of the sodium derivative had disappeared, but the ether, on evaporation, left a considerable quantity of unchanged chloride. The heating was continued, small quantities of the sodium derivative being added from time to time, until the reaction remained faintly alkaline after all of the sulphone chloride had disappeared. One gram-molecule of the sulphone chloride required slightly more than 1.5 gram-molecules of the sodium derivative for complete reaction. The reaction-products were treated in various ways, in successive experiments, but as the substances obtained were always the same the following method of separation was adopted as the best: The contents of the flask were filtered, the insoluble sodium salts repeatedly extracted with ether, the ethereal solutions combined, and solution and solid treated separately.

The solid was boiled with absolute alcohol, which left only sodium chloride undissolved. The alcoholic solution, on cooling, deposited pure sodium toluenesulphinate. This was identified by analysis and by the melting-point of the acid obtained by acidifying the salt with hydrochloric acid.

I. 0.1674 gram substance gave 0.0654 gram Na_2SO_4.

II. 0.1829 gram substance gave 0.0721 gram Na_2SO_4.

	Calculated for $C_7H_7SO_2Na$.	Found. I.	Found. II.
Na	12.9	12.65	12.8

The melting-point of the acid was 85°.

The mother-liquor from the sodium sulphinate contained another sodium salt that was much more readily soluble in cold, absolute alcohol. This was purified by solution in cold alcohol and precipitation with ether.

I. 0.1480 gram substance gave 0.0407 gram Na_2SO_4.

II. 0.1759 gram substance gave 0.0430 gram Na_2SO_4.

	Calculated for $C_{11}H_{13}SO_4Na$.	Found. I.	II.
Na	8.7	8.9	8.7

The substance is sodium paratoluenesulphonacetic ester. The aqueous solution was boiled with sodium carbonate and acidified, when it gave an acid melting at 118°. When this was boiled with alkalies it gave methyltolylsulphone melting at 88°. The product insoluble in ether contained no other organic substances. The amount of sodium chloride corresponded to 66 per cent of all the chlorine added, the sodium sulphinate represented 70 per cent, and the toluenesulphonacetic ester about 22 per cent of the sulphone chloride used.

The ethereal solution was acidified with dilute acetic acid, thoroughly washed with water, and dried with anhydrous sodium sulphate. After removing the ether, the residue was subjected to distillation under diminished pressure. It was thus separated into three portions: 1. A very low-boiling fraction composed of ethyl acetate, alcohol, and acetic acid; 2. A fraction that distilled over between 90° and 110° under a pressure of about 30 mm.; and 3. A fraction that could not be distilled without decomposition. The second fraction was changed into copper salts by the method of Wislicenus,[1] and the salts separated by recrystallization from carbon disulphide. Two salts were obtained, copper acetoacetic ester melting at 192°, and copper chloracetoacetic ester, identified by comparison with a specimen prepared from chloracetoacetic ester by the same method.

The third fraction solidified almost completely on standing. It was dried on a plate and repeatedly recrystallized from a mixture of ether and ligroin. It was thus separated into two substances, one of which was paratoluenesulphonacetic ester melting at 118°. The other substance melted at 69°, and gave the following results on analysis:

I. 0.2241 gram substance gave 0.4560 gram CO_2 and 0.1767 gram H_2O.

II. 0.2515 gram substance gave 0.5146 gram CO_2, and 0.1955 gram H_2O.

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[1] Ber. d. chem. Ges., 31, 3151.

	Calculated for $C_{12}H_{18}O_6$.	Found. I.	II.
C	55.81	55.5	55.8
H	6.97	7.1	7.0

The analysis, melting-point, and other properties showed that the substance is diacetosuccinic ester. That this is a secondary product due to the action of sodium acetoacetic ester on chloracetoacetic ester could be shown very clearly by varying the relative amounts of the reagents, and the time of heating. If the reaction was completed in a short time by using a considerable excess of sodium acetoacetic ester very little diacetosuccinic ester was obtained. With smaller quantities of sodium acetoacetic ester and more prolonged heating, on the other hand, very little chloracetoacetic ester remained, the principal products being the sulphinate and diacetosuccinic ester.

Sodium Malonic Ester and Paratoluenesulphone Chloride.

Since sodium malonic ester cannot be isolated in a pure condition, it was necessary to use malonic ester and sodium or malonic ester and sodium ethylate. In the earlier experiments malonic ester in benzene solution was treated with the calculated amount of metallic sodium, and the mixture allowed to stand until all of the sodium had disappeared.[1] A benzene solution of the sulphone chloride was then added, and the mixture heated on the water-bath until all the sulphone chloride had entered into reaction. It was found, however, that the protracted heating, required to complete the reaction in benzene solution, gave rise to so many secondary reactions that it was difficult to isolate pure substances from the products. It was found, also, that 1 molecule of sodium malonic ester is insufficient to react with 1 molecule of the sulphone chloride. Ether was, therefore, substituted for benzene, and sodium alcoholate for metallic sodium.

With 1 molecule of malonic ester, 1 molecule of the sulphone chloride, and sufficient sodium alcoholate to bring all of the sulphone chloride into reaction, the principal products are sodium chloride, sodium toluenesulphinate, and ethyl ethylenetetracarbonate.

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[1] Conrad: Ann. Chem. (Liebig), **204**, 129.

Two and a half grams of sodium were dissolved in 6 grams of absolute alcohol and the mixture diluted with 150 cc. of ether; 20 grams of paratoluenesulphone chloride, dissolved in 200 cc. of ether, were added to this solution, and the whole boiled for three hours. Sodium alcoholate was then added in small portions, and the boiling continued until no sulphone chloride was left. The ether was removed by distillation, and the residue poured into water. The oil that separated was washed with water and dried on the water-bath. After standing for a few days it partially solidified in consequence of the separation of long, colorless needles. These, when purified by recrystallization from boiling water, melted at 79°. They were identified as ethyl ethylenetetracarbonate by comparison with a specimen prepared by treating chlormalonic ester with sodium malonic ester.

The oil from which the crystals had separated gave a good qualitative test for sulphur and chlorine. It could not be distilled in a vacuum, was not volatile with water-vapor, and gave no copper salts; hence its further separation was not attempted.

The aqueous solution was evaporated to dryness and extracted with absolute alcohol. The first crop of crystals from the alcoholic solution was sodium toluenesulphinate.

0.1522 gram of salt gave 0.0593 gram of Na_2SO_4.

	Calculated for $C_7H_7SO_2Na$.	Found.
Na	12.9	12.7

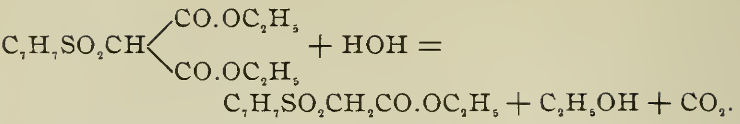
The filtrate from the sulphinate gave a considerable quantity of sodium tolueneacetic ester.

I. 0.1343 gram substance gave 0.0370 gram Na_2SO_4.

II. 0.1599 gram substance gave 0.0439 gram Na_2SO_4.

	Calculated for $C_{11}H_{13}SO_4Na$.	Found.	
		I.	II.
Na	8.7	8.86	8.88

It will be shown below that this substance is formed by the action of sodium toluenesulphinate on chlormalonic ester, the intermediate toluenesulphonmalonic ester being decomposed according to the equation:



$$C_7H_7SO_2CH\left\langle\begin{matrix}CO.OC_2H_5\\CO.OC_2H_5\end{matrix}\right. + HOH = C_7H_7SO_2CH_2CO.OC_2H_5 + C_2H_5OH + CO_2.$$

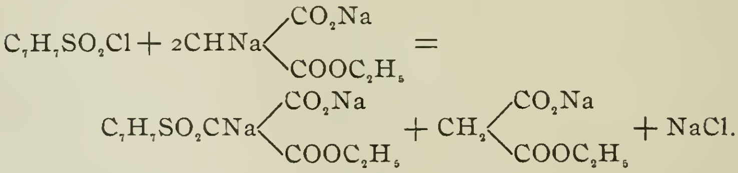
Paratoluenesulphone Chloride and Disodium Malonic Ester.

Two atoms of sodium were dissolved in the minimum amount of absolute alcohol and 1 molecule of malonic ester added to the well-cooled solution. The mixture was shaken until the sodium derivative began to separate, when 1 molecule of the sulphone chloride, dissolved in absolute alcohol, was added. The reaction was complete in twenty minutes. From the alcoholic solution ether precipitated a sodium salt, which after purification from alcohol gave the following results:

0.1547 gram substance gave 0.0662 gram Na_2SO_4.

	Calculated for $C_{11}H_{12}SO_6Na$.	Found.
Na	13.9	13.8

The composition of the substance corresponds to that of an ester salt of toluenesulphonmalonic acid. Its formation is explained by the observation of Bischoff,[1] that disodium malonic ester gives condensation-products derived from an ester salt of malonic acid:



$$C_7H_7SO_2Cl + 2CHNa\left\langle\begin{matrix}CO_2Na\\COOC_2H_5\end{matrix}\right. = C_7H_7SO_2CNa\left\langle\begin{matrix}CO_2Na\\COOC_2H_5\end{matrix}\right. + CH_2\left\langle\begin{matrix}CO_2Na\\COOC_2H_5\end{matrix}\right. + NaCl.$$

The properties of the substance agree with the formula given. On acidifying its solution in water, carbon dioxide was given off and a substance, difficultly soluble in water, separated out. After purification this melted at 94° and gave the following analytical results:

I. 0.1434 gram substance gave 0.2864 gram CO_2, and 0.0642 gram H_2O.

II. 0.1180 gram substance gave 0.2351 gram CO_2, and 0.0516 gram H_2O.

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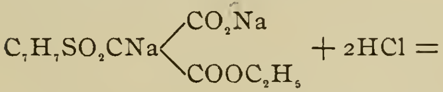
[1] Ber. d. chem. Ges., **17**, 2782.

	Calculated for $C_{11}H_{14}SO_4$.	Found. I.	II.
C	54.54	54.46	54.33
H	5.79	5.0	4.85

The substance is paratoluenesulphonacetic ester, formed according to the equation :



$$C_7H_7SO_2CNa\left\langle\begin{matrix}CO_2Na\\ COOC_2H_5\end{matrix}\right. + 2HCl = \\ C_7H_7SO_2CH_2COOC_2H_5 + CO_2 + 2NaCl.$$

Sodium Toluenesulphinate and Chloracetoacetic Ester.

Some years ago Otto[1] studied the reaction between sodium benzenesulphinate and chloracetoacetic ester, and expressed the results by the equation :

$$CH_3COCHClCOOC_2H_5 + C_6H_5SO_2Na + H_2O = \\ C_6H_5SO_2CH_2COOC_2H_5 + CH_3COOH + NaCl,$$

assuming the intermediate formation of phenylsulphonacetoacetic ester. Otto's experiments do not show at what stage acetic acid is split off, hence they were repeated with paratoluenesulphone chloride using absolute alcohol, ether, or benzene as a medium. It was found that the substances do not react at all in absolute ether and benzene. In absolute alcohol they react very readily but the odor of ethyl acetate soon becomes perceptible, even if the mixture is allowed to stand in the cold. If the reaction is completed without warming, it takes place almost quantitatively according to the equation :

$$C_7H_7SO_2Na + CH_3COCHClCOOC_2H_5 + C_2H_5OH = \\ NaCl + CH_3COOC_2H_5 + C_7H_7SO_2CH_2COOC_2H_5.$$

Eighteen grams of sodium toluenesulphinate were dissolved in 100 cc. of absolute alcohol and 17.5 grams of chloracetoacetic ester added. The mixture was allowed to stand in a tightly-corked flask for two weeks. The alcohol and ethyl acetate were then removed by drawing a rapid current of dry air through the liquid under greatly diminished pressure. The residue solidified completely, one recrystallization from ether gave

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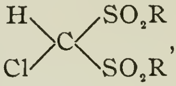
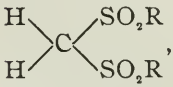
[1] Ber. d. chem. Ges., 23, 756.

21.8 grams of pure paratoluenesulphonacetic ester instead of 24.2 grams calculated.

If the alcoholic solution of the substances is warmed on a water-bath, an entirely different reaction takes place; very little ethyl acetate and toluenesulphonacetic ester are obtained, most of the sulphinate being oxidized to sulphonate, and most of the chloracetoacetic ester reduced to acetoacetic ester.

Seventeen and a half grams of chloracetoacetic ester were added to a solution of 18 grams of sodium toluenesulphinate in 50 cc. of boiling absolute alcohol. At first only sodium chloride separated, but after boiling for a few minutes the liquid became strongly acid and sodium toluenesulphonate began to crystallize out in characteristic plates. After boiling for about half an hour the alcohol was removed and the residue extracted with ether. The ethereal solution was washed with sodium carbonate, the ether removed by distillation, and the residue treated with copper sulphate and ammonia. It gave 11.8 grams of pure copper acetic ester, and a small quantity of copper chloracetoacetic ester. The sodium carbonate washings gave 4.5 grams of toluenesulphinic acid along with a trace of acetic acid.

The residue, insoluble in ether, was treated with absolute alcohol. It contained 15.8 grams of sodium toluenesulphonate. These results show that most of the sulphinate is oxidized at the expense of the chloracetoacetic ester. A similar reduction, in the case of chlorine substitution-products of disulphones, was observed by Fromm,[1] who found that when chlorinated disulphones of the type  $\begin{matrix}H\\Cl\end{matrix}{>}C{<}\begin{matrix}SO_2R\\SO_2R\end{matrix}$, are treated with potassium hydroxide, 1 molecule is reduced to  $\begin{matrix}H\\H\end{matrix}{>}C{<}\begin{matrix}SO_2R\\SO_2R\end{matrix}$, while another is decomposed, the sulphone groups being split off and oxidized to sulphonates or even sulphates.

In the experiments described above, the chlorketonic ester,

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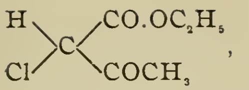
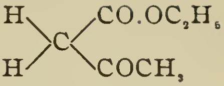
[1] Ber. d. chem. Ges., **21**, 185.


, is reduced to

, by a sulphinate and alcohol.

The experiments were repeated with chlormalonic ester and chloracetylacetone with exactly similar results. In each case the course of the reaction depends upon the temperature and the concentration. In the cold and in dilute solution an acetyl or a carboxethyl group is replaced by the sulphone group; in boiling concentrated solution the sulphonate is oxidized, and the chlorester or ketone reduced. In boiling dilute solutions the two reactions take place at the same time.

Sodium Chloracetoacetic Ester and Sodium Toluenesulphinate.

The instability of substances like benzoylacetoacetic ester and benzoylacetylacetone is generally attributed to the accumulation of negative groups. Assuming this explanation to be correct, it seemed possible that the stability might be increased by the introduction of a positive metallic atom. This led to attempts to prepare a metallic derivative of paratoluenesulphonacetoacetic ester by starting with copper or sodium chloracetoacetic ester and the sulphinate. It was found that the copper compound could not be used, because it immediately reacted with the sodium sulphinate to form the sodium derivative of the chlorester and oxidation-products of the sulphinic acid. Sodium chloracetoacetic ester is much less reactive than the free ester, and can be used with advantage in the preparation of cyanacetoacetic ester and similar substances, but in the reaction under consideration it gives no better results. The only difference observed was that, in the case of the sodium derivative, there is very little oxidation of the sulphinate, the main products under all conditions being sodium chloride, sodium paratoluenesulphonacetic ester and ethyl acetate.

Sodium Acetoacetic Ester and Paratoluenethiosulphonic Ester.

A mixture of equivalent quantities of the substances in a large amount of absolute ether was warmed in a water-bath. At first only sodium sulphinate separated, but after heating for several hours a hard, granular deposit began to form on the sides of the vessel. The heating was continued until this deposit no longer increased in amount—usually from thirty to forty hours. The ethereal solution was then poured off and the solids separated mechanically.

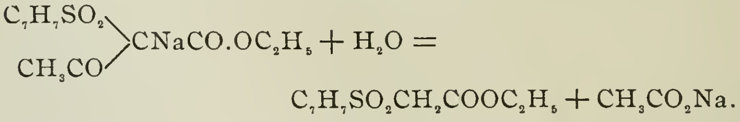
The ethereal solution contained only acetoacetic ester. The flocculent precipitate was dissolved in water, acidified with acetic acid, and distilled with steam. The distillate contained ethylmercaptan identified as the copper derivative. The residue, after distillation, was acidified with dilute sulphuric acid, when paratoluenesulphinic acid separated. The granular deposit was washed with ether, rapidly dried at 50°, and analyzed.

I. 0.1620 gram substance gave 0.0390 gram Na_2SO_4.

II. 0.2673 gram substance gave 0.0649 gram Na_2SO_4.

	Calculated for $C_{13}H_{15}SO_5Na$.	Found. I.	Found. II.
Na	7.52	7.8	7.9

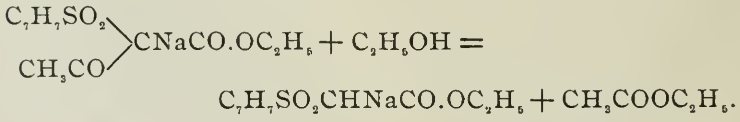
The substance is so extremely unstable that it was impossible to free it from small quantities of mercaptide and sulphinate; but its properties show clearly that it is sodium toluenesulphonacetoacetic ester. It dissolves in water to form a neutral solution which almost immediately becomes acid. In a few minutes paratoluenesulphonacetic ester begins to crystallize out. If the aqueous solution is acidified with dilute sulphuric acid the separation is immediate and complete:



$$\left.\begin{matrix} C_7H_7SO_2 \\ CH_3CO \end{matrix}\right> CNaCO.OC_2H_5 + H_2O = C_7H_7SO_2CH_2COOC_2H_5 + CH_3CO_2Na.$$

One and a half grams of substance gave 1.05 grams of toluenesulphonacetic ester instead of 1.21 grams calculated.

When treated with cold absolute alcohol, the odor of ethyl acetate soon becomes perceptible, and the granular solid swells up in passing into the bulky sodium toluenesulphonacetic ester:



$$\left.\begin{matrix} C_7H_7SO_2 \\ CH_3CO \end{matrix}\right> CNaCO.OC_2H_5 + C_2H_5OH = C_7H_7SO_2CHNaCO.OC_2H_5 + CH_3COOC_2H_5.$$

With aqueous and alcoholic potash the substance gives tolylmethylsulphone, but not a trace of sulphinate or sulphonate, showing that the sulphinate obtained in the reaction between sulphone chlorides and metallic derivatives is a primary product. It will be observed that all the reactions of the substance are analogous to those of benzoylacetoacetic ester, the only difference between the two being the greater reactivity of the former.

The yield of the substance is always exceedingly small. The most favorable results were 2 grams of substance from 30 grams of sodium acetoacetic ester.

BRYN MAWR COLLEGE,
June, 1899.

NOTES.

The Boiling-point of Liquid Hydrogen as Determined by a Rhodium-platinum Resistance Thermometer.

In a recent number of the Proceedings of the Chemical Society there is an interesting note on the above subject by Professor Dewar which is here for the most part reprinted : Within the last week the author has succeeded in obtaining 250 cc. of colorless liquid hydrogen, and this has been employed in a redetermination of the boiling-point. Earlier observations made with a pure platinum resistance thermometer have given —238° as the boiling-point, and a new thermometer constructed from pure platinum from a different source gave practically the same result. As this might be affected by some constant error, the determination was checked by employing a thermometer constructed from an alloy of rhodium and platinum, containing 10 per cent of the former. Alloys had been shown by Professor Fleming and the author to differ from pure metals in showing no sign of becoming perfect conductors at the absolute zero of temperature, and a study of the rhodium-platinum alloy had shown that the change in conductivity produced by cooling from 0° to the boiling-point of liquid air is regular, and may be represented by a straight line. As determined by the rhodium-platinum thermometer the boiling-point of hydrogen was found to be —246°. Two ways of explaining the discrepancy between the two determinations suggested themselves. Pure platinum, although its resistance may be represented by a straight line almost down to the solidifying point of air shows signs of a departure from regularity at about this point, and the curve may become asymptotic at lower temperatures. On the other hand, the resistance of the rhodium-platinum alloy diminishes less rapidly at these lower temperatures and is much higher than that of pure platinum under similar conditions. It follows that its resistance-temperature curve, in all probability, deviates less from a straight line than is the case with platinum. Either cause would explain the differences observed, but the lower boiling-point, —256°, or 27° absolute, seemed to be the more probable, as it agreed very fairly with the value for the boiling-point calculated by the author from Wroblewski's results and that arrived at by Olszewski. As the use of other pure metals could not lead to more satisfactory results, the problem must be attacked in a different way by means of an "air" thermometer containing hydrogen under diminished pressure.

Addendum.—Since this paper was communicated, the author has made a first attempt at determining the boiling-point by a constant volume hydrogen thermometer working under diminished pressure. The result is that this thermometer, which gave the boiling-point of oxygen as 90.5° absolute, or —182.5°, gave for hydrogen, 21° absolute, or —252°. The three determinations that have been made are then as follows: (1) Pure platinum resistance thermometer, 35° absolute; (2) rhodium-platinum resistance thermometer, 27° absolute; (3) hydrogen thermometer, 20° absolute. From this it appears that the boiling-point of hydrogen is really lower than was anticipated. The experiment will be repeated with thermometers fitted with hydrogen prepared from different sources. The boiling-point should be determined by the use of a hydrogen thermometer fitted with gas obtained from the evaporation of the liquid hydrogen itself.

On the Blue Color of Water.

In an article that appeared in No. 1, Vol. XVIII, of the Receuil des Travaux Chimiques des Pays-bas et de la Belgique, W. Spring again discusses the question as to the cause of the blue color of water. Many physicists have regarded the blue color of the sea and of lakes as not belonging to the water itself, but as being produced by the reflection of the sunlight from invisible particles which the water always contains in suspension. This idea was suggested by the theory then held regarding the cause of the blue color of the sky. Earlier experiments of Spring led him to the conclusion that water itself is blue, and that the fine particles which it holds in suspension, while contributing very much to its illumination, exert no appreciable influence on the intensity of the blue color. Soret had previously, in 1869, expressed this same opinion. As neither the work of Soret nor that of Spring appears to have convinced every one, Spring has again taken up the subject with the object of determining experimentally the optical properties of the particles contained in clear waters. Parallel rays from a powerful electric light were passed through (1) distilled water, (2) the drinking water of Liège, and (3) rain water that had been allowed to stand. In all cases the presence of particles became apparent, the clearest being the drinking water. There was no evidence of a blue color. Now four experiments were performed :

1. A cell containing a solution of magenta was interposed between the source of light and the tube containing the water, so that only red light passed through the latter. Under these conditions the light appeared red and its intensity was not diminished.

2. The light was passed through a solution of picric acid before it was passed through the water. The yellow light was not in the least modified by being passed through the water.

3. The water was illuminated by blue light produced by interposing a cell containing an ammoniacal solution of cupric hydrate or a piece of cobalt glass. The result was the same as in the first two experiments. The color was not changed by passing the light through the water.

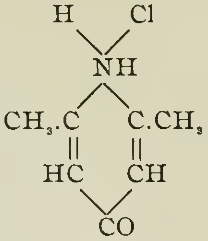
4. Green light produced by passing it through a solution of nickel chloride gave the same results, that is to say, the color was not changed.

These experiments show that the particles, to which clear water, distilled or natural, owes its illumination, have the power to reflect the red, the yellow, and the green waves, and that they cannot, therefore, be the cause of the blue color of water. Reflecting with equal facility waves of all lengths, they return the sunlight to us without chromatic change. The author concludes that water is blue of itself, and that the particles which it holds in suspension are the principal cause of its illumination. According to their nature, they determine also the modification of the color of the water, and produce greenish tones when they do not destroy all the natural color. I. R.

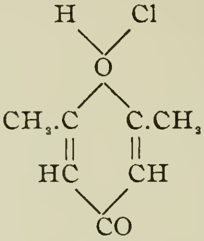
REPORT.

Quadrivalence of Oxygen.

In a recent paper[1] Collie and Tickle call attention to a number of reactions which can hardly be explained without assuming the quadrivalence of oxygen. In working with dimethylpyrone they obtained a substance, by the action of hydrochloric acid on it, which acted in a very peculiar manner. It behaved as an easily dissociated salt of a strong acid and weak base would behave, the dimethylpyrone being the basic substance. Further work showed that similar salts could be obtained with a number of acids. The easy breaking down into hydrochloric acid and dimethylpyrone when the salt is dissolved in water, and the decomposition of the other salts cannot be explained if the structure is as represented by the usual formula. If, however, these compounds are regarded as analogous to those formed by dimethylpyridone, the decompositions can be readily explained.



Dimethylpyridine
hydrochloride.



Dimethylpyrone
hydrochloride.

The authors point out that this necessitates the assumption of the quadrivalence of oxygen, a view which is, however, supported by other evidence. Methylic ether hydrochloride, ethyl peroxide, and other compounds are considered by some to contain quadrivalent oxygen. Nef has called attention to similar cases in the peroxidized compounds studied by him, and Brühl has found that the results obtained in studying the refraction of hydrogen peroxide and water lead to the view that in these compounds the oxygen is quadrivalent. This has also served to explain the difference between such peroxides as MnO_2 and BaO_2, on the one hand, and CO_2 and SO_2 on the other. Oxygen also, as a typical element, might be expected to show a dual valency similar to its neighbors—nitrogen, sulphur, and phosphorus. We would expect this power to be weak and only shown in special cases. If oxygen is quadrivalent it may explain the great activity of oxygen compounds. This may be due to the residual unsatisfied affinity, and the action in the case of alcohol, for example, may take place thus:

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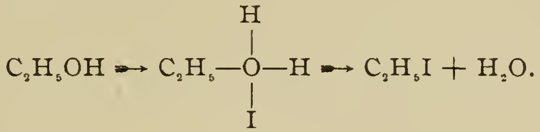
[1] J. Chem. Soc., 75, 710.



$$C_2H_5OH \rightarrow C_2H_5\text{—}\overset{\overset{H}{|}}{\underset{\underset{I}{|}}{O}}\text{—}H \rightarrow C_2H_5I + H_2O.$$

Many reactions, as the oxidation and reduction of hydrogen peroxide, the formation either of *o*-, *m*-, or *p*-substituted compounds from oxygenated benzene compounds, and also etherification and hydrolysis, might be explained on such a basis. If oxygen can replace phosphorus, nitrogen, or sulphur in bases, these oxygen compounds can be regarded as derivatives of OH_3OH, as phosphorus compounds are derived from PH_3OH and nitrogen compounds from NH_4OH. J. E. G.

REVIEWS.

A LABORATORY OUTLINE OF GENERAL CHEMISTRY. By ALEXANDER SMITH, Chicago. Kent Chemical Laboratory of the University of Chicago. 1899.

The author begins his preface with these words: "No apology is offered for the preparation of another laboratory manual. Each teacher of chemistry sooner or later catches the infection, and finds himself impelled to prepare an outline of his own. There is little material that is original in the present one. The author therefore acknowledges his indebtedness to other similar outlines. Ramsay's 'Experimental Proofs of Chemical Theory' may be named as the source of some of the quantitative experiments."

Further on he says: "The work outlined is designed to occupy about six hours of laboratory work per week for nine months." The time required is the maximum that can well be required in a college course in chemistry, and there are probably but few colleges in the country where courses as full as this are given, or can well be given under existing conditions.

The course involves more quantitative work than usual, and there can be no doubt of the value of this kind of work. It takes time, especially if well done, and, if not well done, its value is much less; it may be even injurious. Some of the quantitative experiments described are no doubt capable of giving good results, while of others this cannot be said. One would be inclined to think, for example, that the experiment on multiple proportions, p. 17, might easily miscarry when committed to the hands of the average college student. It may be, however, that all the experiments give excellent results when properly carried out. If so, Professor Smith has contributed something to the cause of laboratory teaching of chemistry.

The course is a "stiff" one, to use the technical adjective. It contains a good deal of detail, covering the field of general chemistry more thoroughly than most of those with which the writer of this notice is familiar.

One feature of the book will attract the attention of every reader, and that is the treatment of the subject of "ionization and interactions of acids, bases, and salts." It seems necessary, in view of the valuable results that have been reached through the study of solutions, that the theory of electrolytic dissociation should be brought to the attention of the student in the early stages of his work. The author recognizes this, and makes an effort to do his duty. Perhaps the work described in Chapter XI will leave a clear impression in the mind of the student, but it is difficult to see how it can, without a great deal of study—not mere reading of brief extracts from Ostwald and Walker.

On the whole, the book is clear and accurate and characterized by a strong infusion of common sense. I. R.

CHEMISTRY AND METALLURGY APPLIED TO DENTISTRY. BY VERNON J. HALL, Ph.D., Professor of Chemistry and Director of the Chemical Laboratories in the Dental School and in the Woman's Medical School of Northwestern University. Evanston, Illinois: The Technical Press. 270 pp. $2.00.

In this book the author has confined himself strictly to the subjects having a bearing on dentistry. The non-metallic elements are not considered at all; but in Part I the general properties of the metals are briefly discussed, with the methods of analyzing mixtures and alloys. Part II contains a description of the general properties, methods of preparing, testing, and analyzing alloys, amalgams, amalgam-alloys, solders, dental cements, and gold, silver, and mercury. The author states in the preface that the student is expected to have received instruction in the elementary principles of chemistry before taking up this course; but it is hardly possible to give so much time to chemistry with the short time allowed for the entire course at most dental colleges. The amount of elementary chemistry taught in such a preliminary course varies in different institutions; but, unless some preliminary training in quantitative methods had been gained, the student would hardly be capable of obtaining the desired results without considerable personal attention from the teacher. J. E. G.

VICTOR VON RICHTER'S ORGANIC CHEMISTRY, OR CHEMISTRY OF THE CARBON COMPOUNDS. Edited by PROF. R. ANSCHÜTZ, University of Bonn. Authorized translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Third American from the Eighth German Edition. Volume I. Chemistry of the Aliphatic Series. With illustrations. Philadelphia: P. Blakiston's Son & Co., 1012 Walnut St. 1899. pp. 626. Price, $3.00.

American chemists again have occasion to thank Professor Smith for preparing a translation of the latest German edition of Von Richter's well-known book, and also Professor Anschütz for his careful editing. As the translator says, "The student of the present edition will * * very quickly discover that the subject matter, so ably edited by Professor Anschütz, is vastly different from that given in the earlier editions. Indeed, the book has sustained very radical changes in many particulars, and certainly to its decided advantage. The book is, of course, characterized by true German thoroughness, while, at the same time, the treatment is systematic, and admirably adapted to the needs of the advanced student. The beginner would have a hard time of it were he to try to get an insight into the system of organic chemistry by the aid of this book, no matter how good a course of explanatory lectures might go with it. If, however, he has begun to see the principles of the system he could hardly find any better book to help him on.

The question of nomenclature is becoming a more and more pressing one in spite of the efforts of the Geneva Congress. The editor has made some use of the new names proposed by the congress, though he has not attempted to introduce and use them consistently. But who has? He says (p. 57): "The new names adopted by the Geneva Commission will, in the case of important series of compounds, be observed in the present text; they will be enclosed in brackets—*e. g.*, [ethene] for ethylene, [ethine] for acetylene, etc." Again, "The principles of this nomenclature have already encountered difficulties, especially in attempting to indicate in name a compound having a mixed character—*e. g.*, the body $COH—CH_2—CHOH—CO—CO_2H$, which would be *pentanolalon acid.*[1] The accumulation of suffixes, each of which possesses a meaning peculiar to itself, has 'conduit rapidement à des termes bizarres, d'une complication facheuse et d'une prononciation difficile' (Amé Pictet)."

Plainly, the only way to avoid the great and increasing difficulties encountered in the nomenclature of organic compounds is to stop making them, and annihilate many of those already made. This, according to a small body of chemists from whom we hear occasionally, would be a boon to chemistry. Of course, compound-making, however low an occupation it may be, is not going to stop. That it is going on in a very rapid way is evident to any one who will take the trouble to look into the subject. This book, covering only one-half of the subject—probably not that—will give the uninformed some idea of the extent of the field already cultivated. Fortunately there is nothing sad and depressing about this. It ought to be, and to many it is, inspiring. For it is only through the collection of material by every possible means that it will ever be possible to discover the possibilities of the chemical elements. Perhaps the most active compound-maker at present is Emil Fischer. Hofmann and Victor Meyer were great compound-makers. So is Von Baeyer, and so are many others of the leaders in chemistry. There are, too, compound-makers who do not contribute very valuable results. But that is the fault of the man, not of the occupation. It will hardly be claimed that all work in other fields of chemistry is necessarily good work.

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[1] This would be *pentanolalonic acid.*—REV.

But enough. Those who have felt called upon to express dissatisfaction with the fact that there is so much activity in field of organic chemistry are advised to give up a sufficient number of years to the study of the subject to justify them in expressing an opinion, and the book that has led to these somewhat inelevant remarks is highly recommended to them as a guide. I. R.

ELECTROLYSIS AND ELECTROSYNTHESIS OF ORGANIC COMPOUNDS. By DR. WALTHER LÖB, Privatdocent in the University of Bonn. Authorized translation from the author's enlarged and revised edition. By H. W. F. LORENZ, A.M., PH.D., graduate of the University of Berlin. First edition, first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1898. pp. 103. Price, $1.00.

The study of the action of the electric current upon organic compounds is not new, as we owe important work in this field to Kekulé and to Kolbe, but it is only within a few years past that such work has been carried on with any activity. Results of value have been obtained, and the author of this book has undertaken to bring together the most important of these.

The book is made up of two parts, entitled, I. *Electrolysis and Electrosynthesis of Aliphatic Compounds*, and II. *Electrolysis and Electrosynthesis of Aromatic Compounds*.

Among the interesting processes described the following may be mentioned:

Iodoform is now manufactured by electrolysis of alcohol in a solution of an alkali iodide.

"If a galvanic current is conducted through acid or neutral aqueous solutions of aniline there is formed at the positive pole, besides other coloring-matters, aniline black, $C_{24}H_{21}N_4Cl$. Under similar conditions dyes are obtained at the positive pole from the salts of *toluidine*, *methylaniline*, *diphenylamine*, *ditolylamine*, and *phenyltolylamine*."

"*Naphthylamine salts* give naphthylamine violet. On electrolysis of *anthraquinone* and potassium hydroxide, Goppelsroeder succeeded in obtaining alivarin."

"According to a patent benzoyl-sulphone-imides can be prepared by the electrolytic oxidation of *toluenesulphone-amides*; for example, *o*-benzoyl-sulphone-imide, or saccharine, from *o-toluene-sulphone-amide*. I. R.

THE SPIRIT OF ORGANIC CHEMISTRY: An Introduction to the Current Literature of the Subject. By ARTHUR LACHMAN (B.S., PH.D.), Professor of Chemistry in the University of Oregon. With an introduction by PAUL C. FREER, M.D., PH.D., Professor of Chemistry in the University of Michigan. New York: The Macmillan Company; London: Macmillan & Co., L't'd. 1899. pp. 229. Price, $1.50.

The author informs us that "This book is intended primarily as a supplement to text-books of organic chemistry." He says, further, "A general principle of organic chemistry, therefore, must be examined by the side of definite experiments—an experiment is the very essence of definiteness. The present state of its development is best discerned by following its historic evolution by a study of its origin and of its career. A number of the chief problems of the science have been taken up in this manner and will be found to answer many of the questions that perplex the rising chemist. Problems which have had no history, which have been established in a single masterly research, manifestly do not fall within the scope of this collection." * * * "Secondly, students are not sufficiently encouraged to read the current literature; and its vastness proves an effective damper if no guide to its mazes be at hand. As most of the subjects selected here are still open questions, as the names of the investigators engaged upon them are prominently put forward, and as the journals in which these chemists are accustomed to publish their results are invariably quoted, no difficulty should be experienced in following up *these* topics at any rate."

The book is, in fact, made up of nine chapters, each of which deals with the development of some interesting and important subject. The titles of the chapters are: The Constitution of Rosaniline; Perkin's Reaction; The Constitution of Benzene; The Constitution of Acetoacetic Ether; The Uric Acid Group; The Constitution of the Sugars; The Isomerism of Maleïc and Fumaric Acids; The Isomerism of the

Oximes; The Constitution of the Diazo Compounds. It is perhaps enough to say that the author has shown clearly that he has grasped the significance of the problems he discusses, and that he undoubtedly has a very thorough knowledge of their literature. Further, he is himself much interested in the work, and, therefore, what he has to say is interesting. His language is in places picturesque, and not always conformable to the rules of grammar. Yet, taking the book as a whole, it can be warmly recommended to students who are trying earnestly to master the principles of organic chemistry.

A few extracts illustrating the author's style are here given: "At about this time (1869), Rosenstiehl found that different rosanilines were obtained according to whether ortho- or paratoluidine were employed for the purpose. These new facts did not collide with the then current theories, however, and Rosenstiehl made no effort to capitalize them. This was reserved for the future."

"The pivotal point, of course, was the recognition of triphenylmethane as the backbone of the group."

"A very limited number of facts had formed the basis of a brilliant and comprehensive generalization. The expectancy of the scientific world was roused to the highest pitch, and with feverish haste and activity all rushed to the chemical Eldorado to participate in its promised wealth of knowledge and insight."

"Kekulé made an attempt to determine the location of substituents by deduction from unfounded general principles."

"After these results the prism formula has not a leg left to stand upon."

"Baeyer studied the reduction products of benzene derivatives, with the idea in mind that the best way to get at the six valences was to put some of them out of the road."

"It supposes that the extra six valences do not directly unite but are attracted toward the center and neutralize each other all of a heap, so to speak."

"From this time on * * * the investigation was of an extremely desultory nature, consisting for the most part of theoretical disquisitions of a reprehensible character."

"At the same time Fischer's "hydrazine" standpoint seemed convincing and final."

"All of a sudden a bombshell was dropped into the diazo camp."

But, assuming this bombshell to have exploded,—though dropping a bombshell into a diazo camp is like carrying coals to Newcastle—the reviewer stops with the remark that any attempt to select all the gems from this book must fail as signally as an attempt to collect all the good things in David Harum.

I. R.

Vol. XXII. October, 1899. No. 4.

AMERICAN

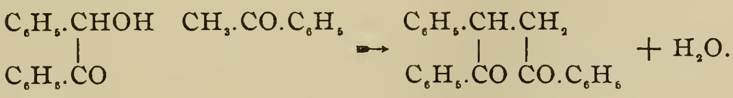
CHEMICAL JOURNAL

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON POTASSIUM CYANIDE AS A CONDENSING AGENT.

By Alexander Smith.

Some years ago I attempted to extend the use of potassium cyanide to other condensations than those resulting in the formation of aromatic ketols like benzoin. These were, at the time, the only cases in which it was effective. It was found that by its agency benzoin[1] and other ketols[2] could be easily combined with ketones, like acetophenone. The substances named gave desylacetophenone:



$$\begin{array}{l} C_6H_5.CHOH \\ \quad\ \ | \\ C_6H_5.CO \end{array} \quad CH_3.CO.C_6H_5 \quad \longrightarrow \quad \begin{array}{l} C_6H_5.CH.CH_2 \\ \qquad\ |\quad\ \ | \\ C_6H_5.CO\ CO.C_6H_5 \end{array} \quad + H_2O.$$

It was also found that benzoin interacted, under its influence, with benzalacetone[3] forming a Δ_2-keto-R-hexane derivative. The latter kind of action was subsequently seen to involve addition of benzoin to the double bond, and subsequent ring formation after the manner of the numerous syntheses carried out by Knoevenagel.[4] It takes place more smoothly when sodium ethylate is used as a condensing agent and has been studied by Dr. J. B. Garner.[1]

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[1] J. Chem. Soc., **57**, (1890) 643.

[2] Ber. d. chem. Ges., **26**, (1892) 60.

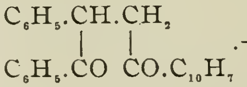
[3] J. Chem. Soc., **57**, 644; Ber. d. chem. Ges., **26**, 70.

[4] Ann. Chem. (Liebig), **281**, (1894) 25.

In 1891 Knoevenagel and Chalanay[2] observed that mandelic nitrile and benzyl cyanide in presence of potassium cyanide reacted to form diphenylsuccinic nitrile, with elimination of water. The former proposed to examine the condensing powers of the same reagent in other directions. On my previous work being brought to his attention, he, very courteously, left the further investigation of the field to me.

One or two aldol syntheses have been carried out with the help of the same condensing agent by Claisen[3] and Kohn[4].

Further experiments in the line originally pursued show that potassium cyanide is not so widely applicable as had been at first expected. In place of benzoin, substances like mandelic nitrile, benzoylcarbinol, furoin, and triphenylcarbinol have been used. For acetophenone there have been substituted acetomesitone, acetonaphthone, benzoylacetone, benzyl cyanide, camphor, fatty ketones, quinaldine, and other substances. The conditions of the experiment (boiling in diluted alcohol) have been altered in various ways. Fusing the substances without solvent and stirring with powdered potassium cyanide has been found frequently to improve the yield. Substitution of powdered potassium hydroxide in the latter method gave excellent results in one or two cases. With most of the possible pairs, from lists like the above, no condensation occurred, or pure products in sufficient amounts could not be isolated. Not wishing any longer to reserve this field, I now publish the few positive results. The 1 : 4 diketones described below were prepared with a view to the study of the action of phenylhydrazine upon them.

Desyl-α-acetonaphthone, 

$$\begin{array}{ll} C_6H_5.CH. & CH_2 \\ \quad\;\; | & | \\ C_6H_5.CO & CO.C_{10}H_7 \end{array}$$

.—The α-acetonaphthone was prepared according to Claus[5] and separated from the β-body by means of the picrates.[6] The ketone (12 grams) and benzoin (17 grams) were dissolved in 50 per cent alcohol (100 cc.), potassium cyanide (2 grams) was added, and the solution was boiled with a reflux condenser for an hour. A turbidity, caused by the separation of an oil, appeared after twenty-five minutes, and, when the solution cooled, most of the product separated as a solid mass. This was extracted three times with boiling alcohol to remove the unchanged materials, and was then dissolved in 3.5 parts of boiling benzene, and precipitated by the addition of petroleum ether (b. p. 40°–60°). The product separated in stellate groups of white needles, which, when purified by repetition of the last process, melted at 151°. The yield was about 7 grams. Another mode of preparation, by fusion in presence of potassium hydroxide, is given below.

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[1] Dissertation, Chicago, 1897.

[2] Ber. d. chem. Ges., **25**, 294.

[3] *Ibid.*, **25**, 3164; Ann. Chem. (Liebig), **306**, 322.

[4] Monatsh. Chem., **19**, 519.

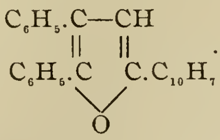
[5] Ber. d. chem. Ges., **19**, 3180.

[6] Rousset: Bull. chim. [3], **17**, 313.

0.1851 gram substance gave 0.5814 gram CO_2, and 0.0958 gram H_2O.

	Calculated for $C_{26}H_{20}O_2$.	Found.
C	85.72	85.66
H	5.50	5.75

The substance is difficultly soluble in boiling alcohol, soluble in 3.5 parts of boiling benzene (less soluble in the cold), and insoluble in petroleum ether. Its constitution as a 1 : 4 diketone was determined by conversion into the corresponding furfurane, pyrrol, and thiophene compounds. The last, made by heating with phosphorus pentasulphide, melted at 93°. It was not analyzed.



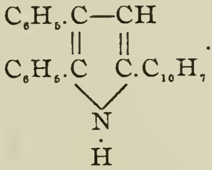
Diphenyl-α-naphthylfurfurane, .—The desyl-α-naphthone (1 gram) was dissolved in cold concentrated sulphuric acid (10 cc.). The solution was allowed to stand for one hour and was then poured into water. The reddish solid which separated was recrystallized from petroleum ether, giving slender white needles melting at 96°.

0.1799 gram substance gave 0.5950 gram CO_2, and 0.0874 gram H_2O.

	Calculated for $C_{26}H_{18}O$.	Found.
C	90.17	90.20
H	5.20	5.40

The substance was difficultly soluble in methyl alcohol, soluble in petroleum ether, very soluble in benzene.

Diphenyl-α-naphthylpyrrol,

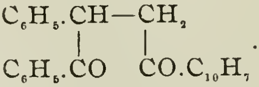


.—The desyl-*α*-naphthone was heated in a sealed tube with ammoniacal absolute alcohol at 200°–220° for eight hours (at 150°–170° little action had been found to take place). The liquid was evaporated and the product taken up with petroleum ether. The dark residue contained unchanged ketone. The solution was once more evaporated and the residue dissolved in alcohol. White needles (m. p. 122°) came out slowly. The substance did not give the red reaction with a pine splinter, but after a time the wood became bluish.

0.1790 gram substance gave 6.6 cc. N over 30 per cent KOH at 21° and 740 mm. (corr.).

	Calculated for $C_{26}H_{19}N$.	Found.
N	4.06	4.11

Desyl-β-naphthone,



$$\begin{array}{ll} C_6H_5.CH & -CH_2 \\ | & | \\ C_6H_5.CO & CO.C_{10}H_7 \end{array}$$

. — The *β*-acetonaphthone (1.8 grams), benzoin (2.3 grams), and potassium cyanide (0.4 gram), were dissolved in 50 per cent alcohol (20 cc.) and boiled with a reflux condenser for one and one-quarter hours. An oil separated and soon became solid. This solid was rubbed repeatedly with cold alcohol and finally freed from impurities by boiling with the same solvent, in which it is soluble with difficulty. The residue was recrystallized three times from benzene and, when pure, formed white needles melting at 155°.

0.1960 gram substance gave 0.6140 gram CO_2, and 0.0990 gram H_2O.

	Calculated for $C_{26}H_{20}O_2$.	Found.
C	85.72	85.43
H	5.50	5.65

It had been hoped that benzoylcarbinol, $C_6H_5.CO.CH_2OH$, on account of its resemblance to benzoin, would interact with acetophenone, and that the constitution of the product would indicate whether the carboxyl or the hydroxyl group of the benzoin is the point attacked. A body melting at 122°–124° was indeed formed, but the yield was too small to permit of further investigation. The other pairs from the lists given above, when any action occurred, failed likewise to furnish products in quantities sufficient for examination.

Syntheses by Fusion with Small Quantities of Potassium Cyanide or Potassium Hydrate.

It was found that fusion, without solvent, of the materials, in presence of powdered potassium cyanide or hydrate, frequently gave excellent yields of the same substances as were obtained by the usual method. The interaction did not start, as a rule, until 150° was reached. At this temperature the action was frequently violent, water vapor, when formed by the action, being given off rapidly.

Benzaldehyde was heated alone to 150°, a little powdered potassium cyanide was added, and the whole was stirred at intervals for forty-five minutes. After remaining over night the residue became solid and gave a good yield of benzoin. Potassium hydroxide gave no benzoin by this method.

Desylacetophenone was prepared by heating molecular proportions of benzoin and acetophenone with a little powdered potassium cyanide at 150° for twenty minutes. Water vapor was given off vigorously. The mass became solid when cold. The yield was 50 per cent of the theoretical. When potassium hydroxide was used in place of the cyanide the same yield was obtained.

The method of boiling the materials in diluted alcohol, as I originally described it,[1] gives a high-melting by-product not formed here, and the yield is only 38 per cent.

Desyl-α-acetonaphthone was easily made by heating molecular quantities of the constituents at 150°, adding a little powdered potassium hydroxide and stirring during fifteen minutes. Water vapor was given off. When the action had ceased and the mass had cooled the solid residue was rubbed repeatedly with cold alcohol and finally recrystallized from benzene. The yield (58 per cent of the theoretical) was better than by the method described above.

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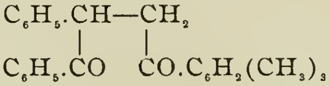
[1] J. Chem. Soc., **57**, 644.

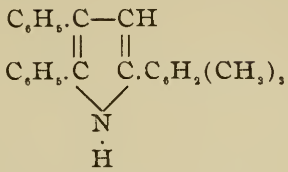
Desylacetomesitone, 
$$\begin{array}{ll} C_6H_5.CH & \!\!\!-\!CH_2 \\ \quad\;\; | & \quad | \\ C_6H_5.CO & CO.C_6H_2(CH_3)_3 \end{array}$$
.—When acetomesitone was boiled with benzoin and a little potassium cyanide in 50 per cent alcohol, most of the material was recovered unchanged. The same result was observed on heating in a sealed tube at 100°. On the other hand, when molecular proportions of the two substances were heated at 150° and powdered potassium hydroxide was added, in small portions at a time, vigorous action took place and water vapor was given off. The action ceased after twenty minutes. The product, after rubbing with cold alcohol, was almost perfectly pure. The yield was 61 per cent of the theoretical. After recrystallization from alcohol it formed white needles which melted at 115°.

0.1422 gram substance gave 0.4384 gram CO_2, and 0.0907 gram H_2O.

	Calculated for $C_{26}H_{24}O_2$.	Found.
C	84.26	84.08
H	6.74	7.09

The substance was soluble in 4.5 parts of boiling alcohol, easily soluble in cold benzene and soluble in boiling petroleum ether (b. p. 40°–60°) from which it crystallized on cooling.

The corresponding diphenylmesitylfurfurane was made by dissolving the ketone in concentrated sulphuric acid, allowing the solution to remain for twenty minutes and pouring the mixture into water. Recrystallized from methyl alcohol, the product formed stellate groups of needles (m. p. 87°). It was soluble in cold petroleum ether.

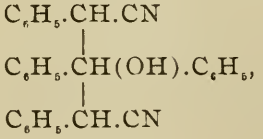
Diphenylmesitylpyrrol,  .— Desylacetomesitone was heated with ammoniacal alcohol in a sealed tube for seven hours at 230°–240°. When the alcohol had been partly distilled off the residue gave white needles melting at 188°.

0.2218 gram substance gave 8.5 cc. N over 30 per cent KOH at 21°.5 and 739 mm. (corr.).

	Calculated for $C_{25}H_{23}N$.	Found.
N	4.15	4.25

Action of Potassium Cyanide on a Fused Mixture of Benzyl Cyanide and Benzoin.

When these substances are boiled with diluted alcohol, the simple condensation that might be expected does not take place. Schleussner,[1] working under the direction of Knoevenagel, found that 2 molecules of benzyl cyanide united with 1 of benzoin, with elimination of 1 molecule of water, to form



$$\begin{array}{l} C_6H_5.CH.CN \\ \quad\quad\;\, | \\ C_6H_5.CH(OH).C_6H_5, \\ \quad\quad\;\, | \\ C_6H_5.CH.CN \end{array}$$

which was the only product.

Heating the substances in equimolecular proportions without solvent and adding powdered potassium cyanide was equally unsuccessful. Instead of a simple condensation-product, four different substances were formed: (1) Schleussner's body mentioned above (m. p. 181°). (2) A body melting at 86°, which was found to be benzalbenzyl cyanide[2] (α-phenylcinnamic nitrile). For the purpose of identification, this was converted into the dibromo-addition-product, which was found to melt at 149°–150°. As Meyer and Frost give the melting-point of the latter 129°–130° (probably a misprint), the nitrile and bromo-derivative were made according to their directions. The agreement in physical properties was complete. (3) A small amount of a yellow amorphous substance not investigated. (4) A substance melting at 227°.5, which was shown by physical properties, nitrogen estimation, and comparison with a sample made in another way, to be diphenylsuccinic nitrile. The melting-point is that of all specimens of the α-form which are not entirely free from the β-variety.

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[1] Inaugural Dissertation; Frankfurt, 1893, p. 11.

[2] V. Meyer and Frost: Ann. Chem. (Liebig), **250**, 157.

I. 0.1890 gram substance gave 20.6 cc. N over 30 per cent KOH at 19° and 745.5 mm. (corr.).

II. 0.1372 gram substance gave 15 cc. N over 30 per cent KOH at 20° and 743.5 mm. (corr.).

	Calculated for $C_{16}H_{12}N_2$.	Found. I.	II.
N	12.07	12.30	12.25

In conclusion, I wish to thank Dr. H. N. McCoy for the able assistance he has rendered in connection with the experimental work described in this paper.

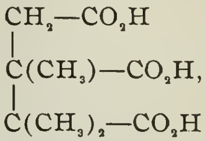
Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XVI.—CAMPHORIC ACID.

[SEVENTH PAPER.]

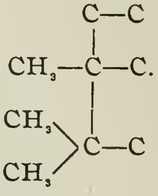
BY WILLIAM A. NOYES.

The synthesis of the inactive camphoronic acid by W. H. Perkin,[1] Jr., demonstrating that it is trimethyltricarballylic acid,



$$\begin{array}{l} CH_2—CO_2H \\ | \\ C(CH_3)—CO_2H \\ | \\ C(CH_3)_2—CO_2H \end{array}$$

has established almost beyond question that camphoric acid and camphor must contain the complex



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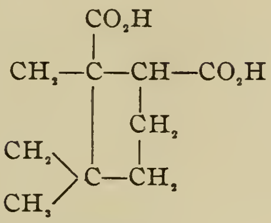
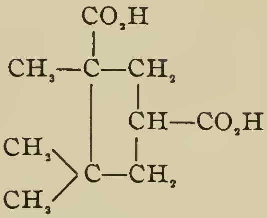
[1] Perkin and Thorpe: J. Chem. Soc., 71, 1169 (1897).

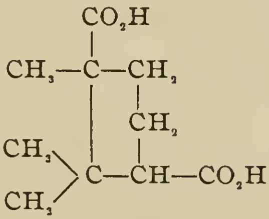
Three formulæ for camphoric acid contain this complex. These are :



Perkin.[1]
(Bouveault.)[2]



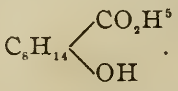
Perkin.[3]



Bredt.[4]

In the first of these formulæ camphoric acid is represented as a derivative of succinic acid, in the other two as a derivative of glutaric acid. The following facts appear to the writer inconsistent with the second and third formulæ.

β-Camphoramidic acid, $C_8H_{14}\left\langle\begin{matrix}CO_2H\\ CONH_2\end{matrix}\right.$, is converted by sodium hypobromite into dihydroaminocampholytic acid. The latter, on treatment with nitrous acid, gives campholytic acid, $C_8H_{13}CO_2H$, and dihydrohydroxycampholytic acid,



$$C_8H_{14}\left\langle\begin{matrix}CO_2H^5\\ OH\end{matrix}\right. .$$

The hydroxyl group of this acid evidently corresponds in position to one of the carboxyl groups of camphoric acid, and must occupy either the β- or γ-position with reference to the carboxyl of the acid. But both campholytic acid and the hydroxy acid pass over into ciscampholytic acid[1] on treatment with dilute sulphuric acid. If the hydroxyl group were in the γ-position with reference to the carboxyl it is very difficult to see why a lactone should not be formed under these conditions, as lactones are readily formed in the camphor series. α-Camphoramidic acid gives with sodium hypobromite aminolauronic acid, $C_8H_{14}\left\langle\begin{matrix}CO_2H\\NH_2\end{matrix}\right.$. The ethyl ester of the latter gives with nitrous acid the esters of γ-lauronolic acid, $C_8H_{13}CO_2H$, and hydroxylauronic acid, $C_8H_{14}\left\langle\begin{matrix}CO_2H\\OH\end{matrix}\right.$[2]. Hydroxylauronic acid, also, does not pass readily into a lactone, although two lactones[3] are known which must contain the same carboxyl as that in this acid. Further, on treatment with potassium pyrochromate and sulphuric acid, hydroxylauronic acid loses carbon dioxide and gives a ketone. This points very strongly to the β-position for the hydroxyl group.

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[1] Proc. Chem. Soc., 1896, 191.

[2] Chem. Ztg., **21**, 761 (1897).

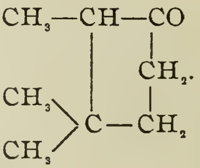
[3] J. Chem. Soc., **73**, 798, 806 (1898).

[4] Ber. d. chem. Ges., **26**, 3049 (1893).

[5] This JOURNAL, **17**, 424.

Entirely independent evidence of the incorrectness of Perkin's second formula will be given in the latter part of this paper.

Some time ago Mr. E. B. Harris and myself obtained a very small amount of a ketone, $C_8H_{14}O$.[4] Recently Mr. J. W. Shepherd and myself have prepared the ketone again, by a different method, and have studied some of its derivatives. If the reasoning given above is correct, this ketone is 2,3,3-trimethylcyclopentanone,



The synthesis of this ketone has acquired, therefore, especial interest. While the synthesis has not yet been effected, the preliminary work is far enough advanced so that its preparation can be considered as reasonably certain. As the material required is not very easily accessible and the completion of the synthesis may take some time, it seems desirable to give an account of the work which has already been accomplished.

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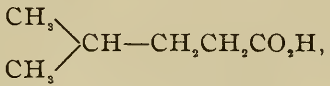
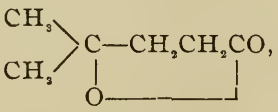
[1] The isolauronolic acid of Koenigs and Hoerlin. See This JOURNAL, **22**, 4.

[2] This JOURNAL, **18**, 687.

[3] Fittig and Woringer: Ann. Chem. (Liebig), **227**, 10; Noyes: This JOURNAL, **17**, 432.

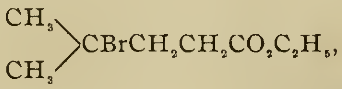
[4] This JOURNAL, **18**, 694.

Amyl bromide, from the amyl alcohol of fusel oil and phosphorus tribromide, was converted into the cyanide and into isocaproic acid,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH-CH_2CH_2CO_2H$, by the usual reactions. From the latter isocaprolactone,



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\underset{\lfloor\!\_\_\_\_ O \_\_\_\_\_\_\_\_\_\rfloor}{C-CH_2CH_2CO},$$

was prepared by oxidation in alkaline solution with potassium permanganate.[1] The methods used in separating the lactone would remove any acids formed from other alcohols than isoamyl alcohol, which might be present in the fusel oil. The ethyl ester of γ-bromisocaproic acid,



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CBrCH_2CH_2CO_2C_2H_5,$$

was prepared by treating the isocaprolactone with alcohol and hydrobromic acid.[2]

? 1.97 grams (1 atom) of sodium was dissolved in 25 cc. of absolute alcohol and 11 grams (cal. 9.7 g. for 1 mol.) of cyanacetic ~~acid~~ were added to the cooled solution. 19.1 grams (1 mol.) of the γ-bromisocaproic ester were then added and the whole was boiled on the water-bath with a reversed condenser for one and a half to two hours. After cooling, the mixture was treated with water and a few drops of sulphuric acid, the products formed were separated from the aqueous solution, and the latter was extracted two or three times with ether. It was found that the brom-ester had been mostly decomposed with the formation of the ester of an unsaturated acid, probably Δ^1-methyl-(2)-pentenoic(5) acid,

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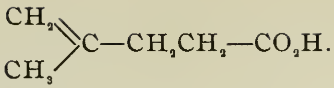
[1] Bredt: Ann. Chem. (Liebig), **208**, 55.

[2] Bredt: Ber. d. chem. Ges., **19**, 514.



$$CH_2{=}C(CH_3){-}CH_2CH_2{-}CO_2H.$$

After distilling this ester and the unchanged cyanacetic ester under diminished pressure, however, a residue remained which mostly solidified on cooling. This residue yielded, on crystallization from alcohol, a little less than 2 grams of a pure substance.

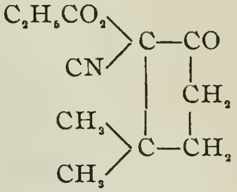
Dimethylcyancarboxethylcyclopentanone, $C_6H_4O(CH_3)_2CN.CO_2C_2H_5$, obtained in this manner, crystallizes from alcohol in colorless needles, which melt at 148°.5. It is rather difficultly soluble in alcohol, almost insoluble in water. It gives no color with ferric chloride.

I. 0.2042 gram of the substance gave 0.1343 gram H_2O, and 0.4726 gram CO_2.

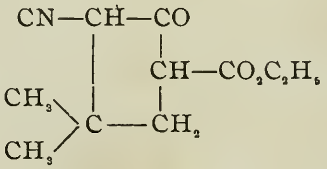
II. 0.994 gram of the substance gave 7.52 cc. of nitrogen at 20°.5 and 585 mm.

	Calculated for $C_{11}H_{15}NO_3$.	Found.	
		I.	II.
C_{11}	63.16	63.12	....
H_{15}	7.18	7.31	....
N	6.70	....	6.80

The structure of the compound may be either



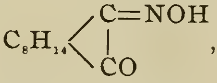
or



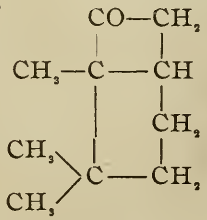
It will probably be possible to decide between these formulæ by the use of the methyl ester of the γ-bromisocaproic acid instead of the ethyl ester. When the substance is heated with water in a sealed tube at 150°–160° for two or three hours the cyanogen group is saponified and eliminated. That the resulting oil is nearly free from nitrogen and that its boiling-point and composition agree approximately with those to be expected for dimethylcarboxethylcyclopentanone has been demonstrated, but the body has not been prepared in pure condition.

By the use of acetoacetic ester in place of the cyanacetic ester, as above, a small amount of an oil boiling at 180°–190° under a pressure of 30 mm. was obtained. Also with methyl malonic ester an oil boiling at 195°–210° (30 mm.) was formed. The yields are in both cases only about 10 per cent of the weight of the brom-ester employed. The use of sodium methyl malonic ester in suspension in benzene did not give a better yield.

It seems probable that from some one of these compounds it will be possible to prepare the trimethylcyclopentanone which is desired.

Some time ago[1] I established the following genetic relationship: α-camphoramidic acid ⟶ aminolauronic acid ⟶ γ-lauronolic acid ⟶ campholactone. Claisen and Manasse[2] have shown that isonitrosocamphor,  $C_8H_{14}\left\langle\begin{array}{l}C{=}NOH\\ |\\ CO\end{array}\right.$, on treatment with hydrochloric acid, passes over into a α-camphoramidic acid. This demonstrates that the carbonyl of camphor corresponds to the carboxyl of aminolauronic acid.

I have also shown[3] that the carboxyl of aminolauronic acid is tertiary while that of dihydroaminocampholytic acid is secondary. If we assume that camphoric acid is a derivative of succinic acid, the formula for camphor which follows is:



This formula was first proposed by Bouveault;[4] though the corresponding formula for camphoric acid had been previously proposed by Perkin (see above). By an unfortunate error the relative positions of the carbonyl and methylene groups are interchanged in the abstract of Bouveault's paper in the Centralblatt, (1897, II, 855).

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[1] This JOURNAL, **17**, 425.

[2] Ann. Chem. (Liebig), **274**, 71; This JOURNAL, **16**, 507.

[3] This JOURNAL, **18**, 686.

[4] Chem. Ztg., **21**, 761.

α-HYDROXYDIHYDROCISCAMPHOLYTIC ACID.

WITH J. W. SHEPHERD.

The ciscampholytic acid required for the preparation of this acid was prepared by the method of Blanc,[1] slightly modified. 25 grams of camphoric anhydride were dissolved in 100 cc. of dry chloroform, slightly warmed; the solution was filtered if not clear; 23 grams of aluminium chloride were added in portions of 4 to 5 grams during a period of five to ten minutes. If the solution warmed at first, the flask was placed in cold water, but very soon the evolution of carbon monoxide became rapid and the solution cooled spontaneously. In order to follow the course of the reaction, the flask was closed with a stopper bearing a delivery tube, and the gas evolved was collected in a large flask over water. When about 4 liters, somewhat more than the theory because of vapor of chloroform, had been collected, and the evolution of the gas had nearly ceased, the chloroform solution was poured into 700 cc. of ice-water, some hydrochloric acid was added, and the aqueous solution was separated and discarded. After washing the chloroform solution a couple of times with water containing hydrochloric acid, an excess of a strong solution of sodium hydroxide was added, and the chloroform was distilled off in a current of steam. After cooling the alkaline solution, the impure ciscampholytic acid was precipitated with hydrochloric acid, filtered off, washed, and dried. Instead of purifying the acid by crystallization or by distilling with steam as recommended by Blanc, it was found much quicker and better to distil it under diminished pressure, using a distilling-bulb to which a wide side-tube was sealed to collect the solid acid. The acid was distilled under a pressure of 30–50 mm., with the oil-bath in which the bulb was heated at about 190°. One distillation gave a pure acid. 150 grams of camphoric anhydride worked up in 6 portions, as described, gave 92 grams of ciscampholytic acid, or 73 per cent of the theoretical yield.

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[1] Bull. Soc. Chim. [III], **15**, 1191. See also Perkin: Jour. Chem. Soc. (London), **73**, 801, 828 (1898).

The ciscampholytic acid was converted into the dihydro acid by reduction with amyl alcohol and sodium.[1] The dihydro acid was converted into the chloride of the α-brom acid by treatment with phosphorus pentachloride and bromine. After distilling away most of the phosphorus oxychloride under diminished pressure, the residue was poured into an excess of absolute alcohol, and the mixture allowed to stand over night. The ester of the α-brom acid was then precipitated by the addition of water.

Thirty grams of the ester were put in a 500 cc. glass-stoppered bottle, with 40–50 grams of crystallized barium hydroxide and 400 cc. of water. Most of the air in the bottle was removed by connecting the lip of the bottle with a wide glass tube by means of rubber tubing, the stopper of the bottle being left loose in the neck. After exhaustion the stopper, which was smeared with a stop-cock lubricant, was jarred into place and the glass tube removed. The removal of the air prevented pressure within the bottle on heating, and also caused a much more thorough mixing of the contents on shaking. The bottle was attached to the fly wheel of a small hot-air motor and shaken continuously for several days. It was also warmed to 30°–40° by placing under it a piece of sheet-iron heated with a Bunsen burner. It is hardly necessary to add that many other methods were tried for the preparation of the hydroxy acid before this one was finally devised.

Even under the conditions described, most of the ester is converted back into ciscampholytic acid. Only about 10 per cent is transformed into the hydroxy acid.

After filtering from unchanged ester the solution was acidified and the precipitated ciscampholytic acid was filtered off at once. The hydroxy acid passed, mostly, into the filtrate and was obtained by repeated extractions with ether. From the precipitated ciscampholytic acid a small amount of the hydroxy acid could be separated by dissolving in the theoretical amount of sodium hydroxide, adding hydrochloric acid for partial precipitation, and distilling away the ciscampholytic acid with steam. Probably the distillation of the ammonium salts with steam would have been better.[2] The hydroxy acid was purified by crystallization from ligroin or benzene.

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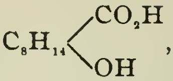
[1] This Journal, **18**, 689 (1896); Perkin: J. Chem. Soc., **73**, 836 (1898).

[2] Perkin: J. Chem. Soc., **73**, 830.

α-Hydroxydihydrociscampholytic Acid,  $C_8H_{14}\begin{cases} CO_2H \\ OH \end{cases}$, crystallizes in needles which melt at 112°. It is difficultly soluble in water and in ligroin, somewhat more easily soluble in benzene.

I. 0.2462 gram substance gave 0.2038 gram H_2O, and 0.5600 gram CO_2.

II. 0.1562 gram substance gave 0.1311 gram H_2O, and 0.3600 gram CO_2.

	Calculated for $C_7H_{16}O_3$.	Found. I.	II.
C	62.79	62.03	62.85
H	9.30	9.20	9.32

Ketone, $C_8H_{14}O$.—This ketone[1] was prepared by distilling the hydroxy acid with lead peroxide and dilute sulphuric acid. 1 gram of the acid, 2 grams of lead peroxide, 4 cc. of dilute sulphuric acid, and 45 cc. of water were put in a distilling bulb, and the mixture distilled very slowly as long as oily drops of the ketone appeared in the distillate. The water was separated from the ketone, the former was returned to the distilling-bulb, more of the acid, lead peroxide, and sulphuric acid were added, and the distillation was continued. 2.5 grams of the acid gave, in this way, about 1 gram of the ketone. In working with larger amounts the yield could probably be increased. The ketone was dried with potassium carbonate and distilled. It boils at 167°–169° and has a specific gravity of $0.8956\frac{20^\circ}{4^\circ}$ or $0.8911\frac{25^\circ}{4^\circ}$. These constants cannot be considered very accurate, as they were determined with a very small amount of the ketone. They are of especial interest for comparison with 3,5-dimethylcyclohexanone, which boils at 181°–182° and has a specific gravity of $0.8994\frac{17^\circ}{4^\circ}$.[2] The lower boiling-point and specific gravity of the ketone from camphor indicate very clearly that it is a derivative of cyclopentanone.

The ketone has a strong odor like that of peppermint and at the same time a musty odor. It is nearly insoluble in water.

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[1] This Journal, **18**, 694.

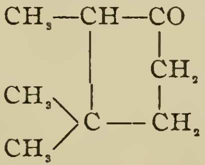
[2] Knoevenagel: Ann. Chem. (Liebig), **297**, 164.

The *oxime*,[1] $C_8H_{14}NOH$, was prepared by adding a strong solution of hydroxylamine chloride and sodium hydroxide to an alcoholic solution of the ketone. It crystallizes from dilute alcohol in needles which melt at 104°. Its odor resembles that of camphoroxime.

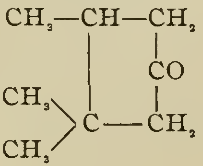
0.1005 gram gave 10.72 cc. of nitrogen at 17° and 634 mm.

	Calculated for $C_8H_{14}NOH$.	Found.
N	9.93	10.17

If Perkin's (Bouveault's) first formula for camphoric acid is correct, the ketone must have the structure designated I below. If the formula at present advocated by Perkin is true, the ketone must have the structure designated II.



I.



II.

A ketone of structure I would condense with 1 molecule of benzaldehyde; one of structure II would condense with 2 molecules.

0.286 gram of the ketone, 0.5 gram of benzaldehyde (2 mols.), 3 cc. of alcohol, and 0.5 cc. of sodium hydroxide (10 per cent) were mixed and allowed to stand over night. There was a slight rise in temperature at first and the reaction was probably complete in a few minutes, and appears to be quantitative. The condensation-product was precipitated with water and taken up with ether. After distilling away the ether, the excess of benzaldehyde was distilled under a pressure of 20–30 mm., the bulb being heated in an oil-bath to 185°. The residue solidified on cooling and weighed 0.393 gram. The theory for a compound formed by condensation with 1 molecule of benzaldehyde is 0.477 gram; with 2 molecules, 0.685 gram. The compound crystallizes from alcohol in needles which melt at 74°. It is difficultly soluble in alcohol, almost insoluble in water.

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[1] This JOURNAL, **18**, 694; **20**, 789.

0.1227 gram substance gave 0.0935 gram H_2O, and 0.3758 gram CO_2.

	Calculated for $C_8H_{12}O{=}CHC_6H_5$.	$C_6H_5CH{=}C_8H_{10}O{=}CHC_5H_5$.	Found.
C	84.11	87.41	83.54
H	8.41	7.28	8.47

The ketone condenses, therefore, with only 1 molecule of benzaldehyde and Perkin's second formula for camphoric acid is, apparently, excluded. These results are consistent with either the first formula of Perkin (Bouveault), or with Bredt's formula. For the reasons given above the former formula appears to the writer more probable.

One-half gram of the ketone was submitted to oxidation with potassium pyrochromate and sulphuric acid, but owing to the small amount of material available, no definite results have been obtained.

Contributions from the Sheffield Laboratory of Yale University.

LXXII.—RESEARCHES ON SUBSTITUTION: THE ACTION OF BROMINE ON METACHLOR-, METABROM-, AND METAIODANILINES.

[SECOND PAPER.]

BY H. L. WHEELER AND WILLIAM VALENTINE.

The action of metasubstituted anilines with chlorine and bromine has been thoroughly investigated only in regard to their behavior on saturation. In each case examined it has been found that the halogens enter the 2, 4, and 6 positions, the meta derivatives behaving, in this respect, precisely like aniline.

With this fact at hand, Langer[1] published the following law: "Dass bei weiterer Substitution des Anilins solche Substituenten, die zur Amido-gruppe die Metastellung einnehmen, gar keinen bemerkbaren Einfluss ausüben und die Zahl der neu eintretenden Halogenatome nicht verringern."

Previously Nölting,[2] in calling attention to this similarity in behavior stated: "Ueberhaupt verhält sich ein bei 3 substituirtes Anilin Agentien gegenüber gerade so wie ein gar nicht substituirtes."

[1] Ann. Chem. (Liebig), **215**, 107.

[2] Ber. d. chem. Ges., **8**, 1093.

These statements are perfectly true when applied in the sense indicated above, but it appears that, with the exception mentioned below, no attempts have been made to determine what the first product is, or what the chief products are when the free anilines are subjected to less energetic treatment.[1] Consequently it has not been shown in what order the different positions 2, 4, and 6 are substituted, and whether or not in these intermediate stages any influence of the substituent in the meta position is to be observed.

Owing to the energy with which the aromatic amines are attacked by chlorine and bromine, and also on account of the formation of by-products, it is customary to moderate the action by employing the acetyl derivatives instead of the free bases. It has been assumed that this procedure simply protects the amino group or moderates the violence of the reaction. Whether in the case of meta substituted anilines it exerts any other influence in the further substitution than this has not been determined, except in the instance described below. In the cases where the acetyl derivatives have been employed it has been found that the substitution takes place smoothly, the halogen entering the position para to the amino group and practically without the formation of by-products. In order to obtain the higher bromine substitution-products the free bases are employed, as, otherwise, the bromination is frequently arrested with the formation of the monobrom derivative, the next step being the formation of perhalides.[2]

Since the question whether a substituent in the meta position influences the further substitution of the aniline had been examined from only one side, one of us investigated the behavior of metanitraniline[3] with bromine, in glacial acetic acid, and found that the nitro group in the meta position exerts not only a protective or retarding influence[4] but also a directing influence on the substitution. The chief product formed was the sweet-tasting 6-brom-3-nitraniline and not the expected

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[1] Beilstein and Kurbatow thoroughly investigated the action of chlorine on metachloracetanilide (Ann. Chem. (Liebig), **196**, 215), but do not mention the action of the free base.

[2] Wheeler and Walden: This Journal, **18**, 25; Wheeler, Barnes, and Pratt: *Ibid.*, **19**, 672.

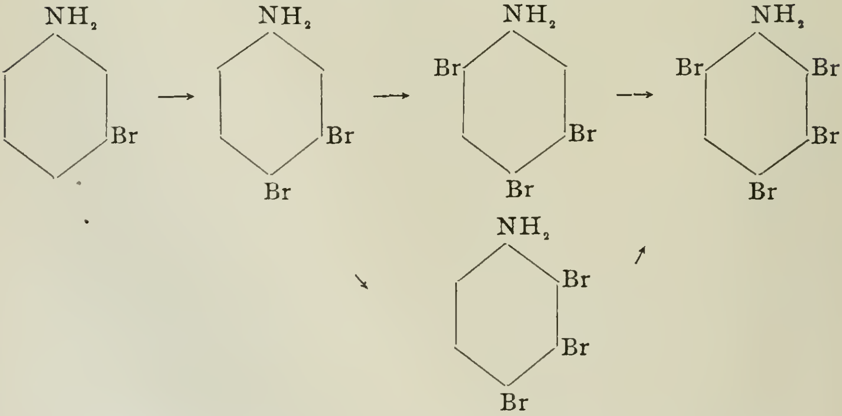
[3] This Journal, **17**, 697.

[4] A fact previously noticed by Michael and Norton (Ber. d. chem. Ges., **11**, 112), in the case of substitution by iodine monochloride.

4-brom-3-nitraniline, which should result from analogy, or if the nitro group exerted no influence. Moreover, it was found that acetylmetanitraniline gave, as the chief product, a different mono derivative, 4-brom-3-nitraniline, than the free base.

We have now extended the examination of meta substituted anilines, and, in this paper, we describe the results of our experiments on the influence exerted when the meta substituent is a halogen, the bromination being conducted as before in a glacial acetic acid solution.[1]

Now, it might be expected that *m*-chlor-, *m*-brom-, and *m*-iodanilines would behave with bromine under similar conditions, like *m*-nitraniline. This, however, is not the case. The chief products formed in the case of the *m*-halogen anilines have been found to be the para derivatives. For example, in the case of *m*-bromaniline (43 grams with 1 molecular proportion of bromine) the product obtained in largest amount was 3,4–dibromaniline (26 grams); next in amount was a mixture of 3,4,6–tribromaniline (in larger amount) with 2,3,4–tribromaniline; then followed 2,3,4,6-tetrabromaniline, from which it follows that the relative tendency of bromine to substitute the hydrogen atoms in these compounds may be expressed in the terms 4>6>2, the course of the reaction proceeding as follows:



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[1] Glacial acetic acid has proved in each case to be well suited for the examination of the lower brominated products. It not only moderates the action less than the acetyl compounds, permitting the examination of the behavior of the free bases, but also simplifies the purification of the products.

The bromination of metachlor- and metaiodaniline gave similar results, the bromine entering the para position to the amino group and forming chiefly a monobrom derivative.

Each of these cases is therefore an exception to the rule of Kehrmann,[1] *i. e.*, that the entering substituent generally takes the ortho position to the substituent of least molecular magnitude.

From the above it is seen that the nitro group in the meta position exerts a different directing influence on the further substitution by bromine than that exerted by the halogens; that the course of the reaction or the energy with which bromination occurs is in opposite directions around the molecules previous to the formation of the final 2,4,6-derivative.

It is well known that the nitro group in nitrobenzene exerts a different directing influence on further substitution from that exerted by the halogens in chlor-, brom-, and iodbenzene. Further substitution in the first case leads to the formation of meta derivatives, while in the latter ortho and para compounds result. The groups, atoms, or radicals that influence the entering substituent to take the ortho or para position have been termed by Lellmann[2] substituents of the *first class*. To this class belong the halogens, the alkyl radicals, and the groups $—NH_2$, $—OH$, $—CH_2R$, while the groups $—NO_2$, $—CO_2H$, $—SO_3H$, etc., which yield meta derivatives on further substitution are known as substituents of the *second class*.

It is suggested by our work so far that a difference in directing influence is still retained by these radicals in the meta-substituted anilines. That, in general, meta-substituted anilines containing substituents of Lellmann's first class will be found to give chiefly a 4-halogen derivative while, on the other hand, those with the radicals of the second class, like metanitraniline, will give a 6-halogen compound as the chief product. We intend to continue the investigation of the influence exerted on the substitution of anilines by groups in the meta position, and we hope, later, to decide the above simple questions which, however, involve considerable work.

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[1] Ber. d. chem. Ges., **23**, 130.

[2] Principien d. Org. Synthese, p. 11.

The Bromination of m-Chloraniline.

When 50 grams of metachloraniline were dissolved in 400 cc. of glacial acetic acid and treated with 62.7 grams of bromine (1 molecule) in the form of vapor, by means of a stream of dry air, a colorless crystalline precipitate separated. This, when dried, weighed 85 grams (Precipitate *A*). It consisted mostly of the mono- and dibrom derivatives in the form of hydrobromic acid salts.[1] The monobrom derivative was extracted by treating this mixture repeatedly with water (Solution *B*), and, on precipitating with ammonia, 35 grams of crude material were obtained.[2]

The treatment with water left the di- and a small amount of tribrom derivatives undissolved, weight 23 grams (Residue *C*). The glacial acetic acid (Solution *A*) was diluted with about three or four times its volume of water, which resulted in the precipitation of the rest of the tribrom derivative[3] (1 gram) in practically pure condition (Precipitate *D*).

The dilute acetic acid solution was then precipitated with strong ammonia, when the unaltered metachloraniline with some monobrom derivative was obtained (Precipitate *E*). The method of examining and purifying these crude products is given below under their separate heads.

The following calculation, being a check on the above weights, confirms the analytical results and the chemical behavior of the products :

		Bromine. Grams.
B	35 grams of monobrom derivative account for	27.1
C	23 " " dibrom " " "	25.8
D	1 gram " tribrom " accounts "	1.3
	Total	54.2

That 8.5 grams of bromine are apparently not accounted for is due to the fact that the monobrom derivative mixed with unaltered *m*-chloraniline (Precipitate *E*) is not included in the above calculation, and also to the fact that the above are

weights of crude products and not of perfectly pure material.

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[1] It also contained the hydrobromic acid salt of unaltered material.

[2] A loss occurs here owing to the solubility of the material in the solutions precipitated by ammonia. As this appeared to be chiefly unaltered material it was not recovered.

[3] Some loss is to be expected here owing to the volume of the solutions.

It is to be expected that the loss in the case of metachloraniline would be greater than with metabromaniline since the chlorine compounds are more soluble. This has been found to be the case, so that the solubility explains a part of this loss. The amount of bromine lost by action on the glacial acetic acid is probably very small. Each one of the brominations described in this paper has been repeated and the results confirmed.

3-Chlor-4-bromaniline.—The precipitate produced by ammonia in Solution *B* was crystallized from dilute alcohol, when four- and six-sided colorless plates separated. They melted constantly from 67°–68°, and a determination of the halogens shows that this material is a monobrom derivative :

	Calculated for C_6H_5NClBr.	Found.
Cl	17.2	17.2
Br	38.7	38.2

The structure is shown by the fact that it gives orthochlorbrombenzene with ethyl nitrite, and since it is formed almost quantitatively by brominating acetyl-*m*-chloraniline, the bromine as usual taking the position para to the acetyl group.

The *hydrochloride*, prepared by passing hydrochloric acid gas into the alcoholic solution of the base, crystallizes in colorless needles. A hydrochloric acid determination gave :

	Calculated for $C_6H_5NClBr.HCl$.	Found.
HCl	15.0	14.6

It is readily soluble in water, less readily in alcohol, and insoluble in benzene. It blackens when heated to about 210°.

The *sulphate* is obtained in the form of colorless plates when the base is treated with dilute sulphuric acid. A sulphuric acid determination gave :

	Calculated for $(C_6H_5NClBr)_2H_2SO_4$.	Found.
H_2SO_4	19.2	19.5

The *picrate* is obtained as a precipitate by adding an alcoholic solution of picric acid to a solution of the base. It crystallizes in yellow needles which melt at 141°. A nitrogen determination gave the following result:

	Calculated for $C_6H_5NClBr.C_6H_3N_3O_7$.	Found.
N	12.9	12.7

1,2-Chlorbrombenzene.—Six grams of the precipitate produced by ammonia in Solution *B* were treated with an excess of ethyl nitrite in the presence of a little concentrated hydrochloric acid. After warming, the material was taken up in ether, washed, dried, and distilled, when 4.5 grams of colorless oil were obtained, boiling from 200°–210°. On redistilling at 772 mm. pressure it all boiled from 201°–204°. It refused to solidify. *p*-Chlorbrombenzene is a solid melting at 67.4°, while the boiling-points of ortho-, meta-, and parachlorbrombenzene are given by Dobbie and Marsden[1] as 204°, 196°, and 196.3°, respectively. Our material is therefore orthochlorbrombenzene.

Nitration of 1,2-Chlorbrombenzene.—In order further to characterize orthochlorbrombenzene we have examined its behavior towards nitric acid. 2 to 3 grams of orthochlorbrombenzene were dissolved in fuming nitric acid and warmed. Water was then added, and the precipitated material, crystallized from 75 per cent alcohol, gave colorless needles melting from 49°–50°. Three crystallizations did not alter the melting-point.[2] A nitrogen determination gave:

	Calculated for $C_6H_3NO_2ClBr$.	Found.
N	5.9	6.3

The structure $C_6H_3NO_2ClBr$,1,4,3, is assigned to this compound, because on reduction it did not give 3-chlor-4-bromaniline, melting at 67°, but a base melting at 75°, after repeated crystallizations. Since, in general, the tendency of ortho compounds, on nitration, is to form an unsymmetrical in preference to a vicinal derivative, it follows that this is in all probability *4-chlor-3-bromaniline.* It was not further examined.

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[1] J. Chem. Soc., 1898, 255.

[2] The true melting-point of 3-brom-4-chlornitrobenzene is probably 60°, the above material being mixed with some 3-chlor-4-bromnitrobenzene.

3-Chlor-4-brom-2,6-dinitraniline.—Eight grams of 3-chlor-4-bromaniline were heated on the steam-bath with concentrated nitric acid. In a few minutes reaction set in with evolution of red fumes. After this was over the solution was diluted with water and the precipitate crystallized from absolute alcohol, in which it is difficultly soluble, when it was obtained in the form of dark-yellow prisms, melting from 169°–170°. A nitrogen determination gave:

	Calculated for $C_6H_3N_3O_4ClBr$.	Found.
N	14.2	14.7

3-Chlor-4-bromacetanilide.—Fifty grams of metachloracetanilide were dissolved in glacial acetic acid, the calculated quantity of bromine was added, and the mixture allowed to stand a few minutes. Water was then added, and the precipitate was crystallized from 50 per cent acetic acid, when it was found to melt sharply at 125°; yield 70 grams, calculated 73 grams. A nitrogen determination gave:

	Calculated for $C_8H_7NOClBr$.	Found.
N	5.6	5.7

The acetyl group is easily removed from this by boiling the alcoholic solution with a little concentrated hydrochloric acid. This gives the hydrochloride of a base which latter is identical in every respect with the monobrom compound formed on brominating *m*-chloraniline.

3-Chlor-4-brom-6-nitroacetanilide.—One part of 3-chlor-4-bromacetanilide is dissolved in 3 parts of cold nitric acid (sp. gr. 1.52) and the solution is allowed to stand for a few minutes. It is then poured into ice-water, and the precipitate, crystallized from absolute alcohol, gives colorless, flattened prisms or plates. These melt from 129°–130°. Yield 7 grams from 5 grams acetyl compound. A nitrogen determination gave:

	Calculated for $C_8H_6N_2O_3ClBr$.	Found.
N	9.5	9.3

3-Chlor-4-brom-6-nitraniline.—Five grams of the above substance were boiled with alcohol containing some concentrated hydrochloric acid when crystalline material began to separate. Water then precipitated the base completely, ammonia giving no precipitate in the filtrate, as the substance is too weakly basic to form a salt under these conditions. It crystallizes from alcohol in long yellow needle-like prisms which melt from 202°–203°. A nitrogen determination gave:

	Calculated for $C_6H_4N_2O_2ClBr$.	Found.
N	11.1	11.0

4-Chlor-3-bromnitrobenzene.—From 2 to 3 grams of the above compound were treated with nitrous acid in alcohol. The material after this treatment was crystallized from alcohol, when light-yellow needles melting at 60° were obtained.

4-Chlor-3-bromaniline.—On reducing the above 4-chlor-3-bromnitrobenzene with tin and hydrochloric acid, a product identical with the base obtained from the nitration of 1,2-chlorbrombenzene should result. This being the case, the structure of this and the four preceding compounds is proved. In fact, a base was obtained which appears to be identical with that described under the head of the nitration of 1,2-chlorbrombenzene. The crude product melted at 75°, but on further crystallizing it was obtained in the form of colorless, shining plates, which melted at 78°. A nitrogen determination gave:

	Calculated for C_6H_5NClBr.	Found.
N	6.8	6.5

3-Chlor-4,6-dibromaniline.—Residue *B* (see above), after being treated thoroughly with water, was crystallized from alcohol, when thin, colorless plates were obtained, melting from 79°–80°. A halogen determination gave:

	Calculated for $C_6H_4NClBr_2$.	Found.
Cl	12.4	12.4
Br	56.0	55.9

3-Chlor-2,4,6-tribromaniline.—On crystallizing Precipitate *C* (see above) from alcohol this compound was obtained. It had all the properties described by Langer.[1]

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[1] *Loc. cit.*

The Bromination of m-Bromaniline.

In one experiment 43 grams of metabromaniline were dissolved in 350 cc. of glacial acetic acid, and 40 grams of bromine (1 molecule) added as described in the previous case. The precipitate produced (*A*) weighed 90 grams. The soluble hydrobromides removed by water and precipitated by ammonia (*B*) weighed 26 grams. The residue (*C*) weighed 16 grams. The precipitate (*D*) produced by water in the glacial acid solution weighed 1 gram, and on filtering from this and adding ammonia practically nothing but unaltered material was found.

The results are checked by the following calculation:

		Bromine. Grams.
B.	26 grams of dibrom derivative account for	17.7
C.	16 " " tribrom " " "	15.5
D.	1 gram " tetrabrom " accounts "	1.1
	Total	34.3

This gives 5.7 grams of bromine not accounted for. It is to be explained in the same manner as the loss in the case of the previous bromination.

3,4-Dibromaniline.—The precipitate by ammonia (*B*), after two crystallizations from 50 per cent alcohol, melted from 80°–81°. It had all the properties of the base produced by reducing 3,4-dibromnitrobenzene.[1]

The *picrate* was obtained by mixing alcoholic solutions of the constituents. The product crystallized from water gave yellow needles, melting at 149°. A nitrogen determination gave:

	Calculated for $C_6H_5NBr_2.C_6H_3N_3O_7$.	Found.
N	11.66	11.7

The *hydrochloride* crystallizes from dilute hydrochloric acid in colorless prisms which decompose when heated from 220°–230°. A hydrochloric acid determination gave:

	Calculated for $C_6H_5NBr_2.HCl$.	Found.
HCl	12.7	12.7

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[1] Korner: Jahresb., 1875, 311.

The *sulphate* crystallizes in colorless plates.

	Calculated for $(C_6H_5NBr_2.)_2.H_2SO_4$.	Found.
H_2SO_4	16.3	16.5

3,4-Dibromacetanilide.—This has recently been prepared[1] by brominating metabromacetanilide. We have prepared it in this way, and also by acetylating precipitate *B*. It crystallizes in slender prisms melting at 128°, as stated by Körner.

3,4,6-Tribromaniline.—When residue *C* (see above) was crystallized from alcohol, colorless needles were obtained which melted from 115°–116°. This proved to be 2,3,4,6-tetrabromaniline. In order to separate this from the tribromanilines the material was taken up in dry ether and hydrochloric acid gas passed in. This produced a precipitate of the hydrochloric acid salts of the tribromanilines, while the tetrabromaniline remained in solution. The precipitate was treated with ammonia and repeatedly crystallized from alcohol, when it melted from 84°–89°; It being still impure it was converted into the acetyl compound. This, on repeated crystallization from alcohol, melted from 188°–189°; on now removing the acetyl group, the free base melted sharply from 85°–86°. A bromine determination in the product melting from 84°–89° gave :

	Calculated for $C_6H_4NBr_3$.	Found.
Br	72.7	72.2

1,3,4-Tribrombenzene.—In order to determine the structure of the above tribromaniline, 1 gram was treated with nitrous acid in alcoholic solution, when a small amount of fine, colorless needles were obtained; these melted from 44°–45°, and were undoubtedly 1,3,-4-tribrombenzene, which forms needles and melts at 44°. The above base, melting at 85°–86° is, therefore, 3,4,6-tribromaniline.

3,4,6-Tribromacetanilide is therefore the compound crystallizing in colorless needles and melting from 188°–189°, as mentioned above. This same compound and the corresponding base were also prepared in the following manner: *p*-Di-brombenzene was nitrated and the product reduced; this gave 3,6-dibromaniline, which melted from 51°–52°, and agreed in properties with Meyer and Stüber's[1] description except that, when sufficiently purified, it does not have the odor of α-naphthylamine. On acetylating, 3,6-dibromacetanilide was obtained.

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[1] Körner : Bull. Soc. Chim. (Paris), 1896, 1047.

3,6-Dibromacetanilide, on crystallizing from alcohol, was found to melt from 171°–172°, and a nitrogen determination gave:

	Calculated for $C_8H_7NOBr_2$.	Found.
N	4.8	4.8

3,4,6-Tribromacetanilide.—The above acetyl compound was dissolved in glacial acetic acid and treated with 1 molecular proportion of bromine, when a product was obtained which crystallized from alcohol in colorless needles and melted from 188°–189°. This is identical in every respect with the acetyl compound obtained from Residue *C*. A nitrogen determination gave:

	Calculated for $C_8H_6NOBr_3$.	Found.
N	3.9	3.8

Here again the different influence of groups in the meta position is to be noticed. The above 3,6-dibromacetanilide is readily attacked by bromine, while 3-nitro-6-bromacetanilide can be crystallized unaltered from pure bromine.

1,2,3-Tribrombenzene.—In another experiment the crude product, *C*, after removal of 2,3,4,6-tetrabrombenzene, was treated directly with nitrous acid, in alcohol, in the presence of hydrochloric acid.[2] On distilling with steam an oil was obtained which, after solidification and crystallization from alcohol, was obtained in the form of colorless plates. These had the odor of the brombenzenes and melted at 85°. Körner[3] gives the melting-point of 1,2,3-tribrombenzene as 87°.4.

It follows, therefore, that the residue *C* consists of 3,4,6-tribromaniline (isolated), 2,3,4-tribromaniline (not isolated), and 2,3,4,6-tetrabromaniline (isolated).

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[1] Ann. Chem. (Liebig), **165**, 180.

[2] These tribromanilines have a great tendency to form orange-colored precipitates (diazoamidobenzenes?) which are decomposed with difficulty by nitrous acid.

[3] Gazz. chim. ital., **4**, 408.

2,3,4,6-Tetrabrombenzene.—The precipitate *D* was found to consist entirely of this. It forms colorless needles, melting from 115°–116°, as described by Körner.[1]

The Bromination of m-Iodaniline.

In one experiment 53 grams of *m*-iodaniline were dissolved in 400 cc. of glacial acetic acid, and 39 grams of bromine were added in the form of vapor. This produced a crystalline precipitate weighing 83 grams (*A*). The material obtained by extracting this with water and precipitating with ammonia (Precipitate *B*) weighed 35 grams. The residue *C* weighed 30 grams, and the precipitate *D*, produced by water in the glacial acetic acid solution, weighed 1 gram. Ammonia added to the filtrate from this gave unaltered material. Checking these weights now by the following calculation we find that:

		Bromine. Grams.
B.	35 grams of monobrom derivative account for	18.7
C.	30 " " dibrom " " "	25.4
D.	1 gram " tribrom " accounts "	1.0
	Total	45.1

This gives an excess of 6.1 grams of bromine. The error lies chiefly in the assumption that *B* consists entirely of monobrom derivative. As it was not free from oil, it must have contained unaltered material which, calculated as monobrom derivative, explains this excess.

3-Iod-4-bromaniline.—Precipitate *B* was crystallized from alcohol, when it was obtained in the form of colorless plates, melting at 77°. A bromine and iodine determination gave the following:

	Calculated for C_6H_5NBrI.	Found.
Br	26.8	27.3
I	42.6	42.3

We proved the structure of this compound in the following manner: 2.5 grams of 6-brom-3-nitraniline (which gives *p*-bromnitrobenzene with ethyl nitrite) were diazotized and the amino group replaced by iodine by means of potassium iodide. The *3-iod-4-bromnitrobenzene* thus produced crystallized from alcohol in four- and six-sided tables, which melt at 95°–96°, and on reduction the material gave a base melting at 77° and having all the properties of the compound obtained by brominating *m*-iodaniline.

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[1] *Loc Cit.*

The *hydrochloride* was made by passing hydrogen chloride into the benzene solution of the base. It crystallizes from alcohol in long, slender, colorless needles, which decompose when heated at about 210°. A determination of the hydrochloric acid gave:

	Calculated for $C_6H_5NBrI.HCl$.	Found.
HCl	10.9	10.6

The *sulphate* crystallizes in colorless plates from dilute sulphuric acid.

	Calculated for $(C_6H_5NBrI)_2.H_2SO_4$.	Found.
H_2SO_4	14.1	14.2

The *picrate* crystallizes from water in yellow needles, which melt from 158°–159°. A nitrogen determination gave:

	Calculated for $C_6H_5NBrI.C_6H_3N_3O_7$.	Found.
N	10.6	10.9

3-Iod-4-bromacetanilide was prepared by acetylating the above base in the usual way. On crystallizing from alcohol it melted from 138°–139°. A nitrogen determination gave:

	Calculated for C_6H_7NOBrI.	Found.
N	4.1	4.2

3-Iod-4,6-dibromaniline.—The residue *C*, which was insoluble in water, on repeated crystallizations from alcohol, separated in the form of long, colorless prisms, melting at 81°. A bromine and iodine determination gave:

	Calculated for $C_6H_4NBr_2I$.	Found.
Br	42.4	42.6
I	33.7	33.6

3-Iod-2,4,6-tribromaniline.—The precipitate *D*, produced by adding water to the glacial acetic acid solution, was crystallized from alcohol, when minute colorless prisms or plates were obtained, melting at 115°–116°. A bromine and iodine determination gave:

	Calculated for $C_6H_3NBr_3I$.	Found.
Br	52.6	52.3
I	27.8	27.8

New Haven, Conn., June, 1899.

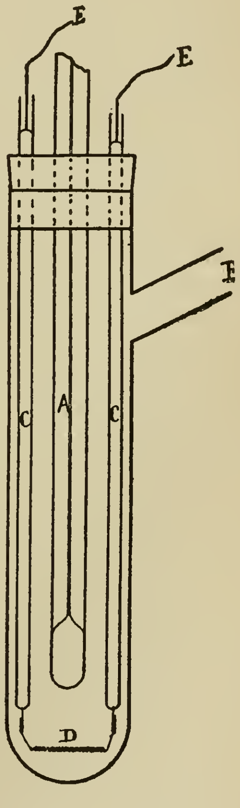
Contribution from the Department of General Chemistry, University of Michigan.

A SIMPLIFICATION OF BECKMANN'S BOILING-POINT APPARATUS.

By S. L. Bigelow.

Most of the attachments to Beckmann's boiling-point apparatus, such as the asbestos stove, the outer mantle containing the boiling solvent, and so forth, have as their object the securing of a constant heating effect, but in spite of these ingenious contrivances the experimenter is left, to a certain extent, at the mercy of changes in the gas-pressure. This difficulty may be avoided, and the whole apparatus be much simplified by using electricity as the source of heat; for example, by passing a current through a fine platinum wire immersed directly in the solution of which the boiling-point is desired. An amperemeter in the circuit gives perfectly reliable data as to the absolute number of heat units furnished to the solution in unit time, and if its readings do not vary, the heating effect must be constant.

Such an arrangement obviates the danger of superheating, for the wire gets so hot that little bubbles of vapor are formed while the body of the liquid is yet far below its boiling-point, and the constant presence of some vapor is well known, both theoretically and practically, to be the best possible precaution against superheating. The platinum wire sealed into the bottom of Beckmann's vessel to facilitate boiling, the glass beads, the asbestos stove, the outer mantle for the boiling solvent, and the return-flow condenser attached to the outer mantle, all become unnecessary. When using low-boiling combustible solvents, such as ether and chloroform, there is relative security from breakage and conflagrations. The cost of the electrical energy is far less than one would at first imagine. As will be seen from the experimental part below, a current of two amperes passing through a resistance of five ohms gives ample heating effect for all ordinary solvents. On the basis of 13.39 cents per thousand watt hours the experiment costs less than one-third of a cent an hour.



The apparatus is shown in the figure. The outer vessel is the same as that used by Beckmann. Later, a large test-tube was substituted for this and, as there was no side arm, the return-flow condenser passed through the cork. The electric connection is furnished by *C*, *C*, two glass tubes filled with mercury, passing through the cork and reaching nearly to the bottom of the vessel. Rather heavy bits of platinum wire are fused into the ends and turned up to form hooks, for convenience in attaching the fine platinum wire destined to do the heating.

The actual diameter of the platinum wire for the heating coil, *D*, is not important, but obviously the greater the diameter the more wire must be used to obtain a given resistance. A meter of wire, 0.1 mm. in diameter, had a resistance of 23+ ohms at room temperature. Tested as to its carrying capacity, it became red-hot with 1.2 amperes passing through it, white-hot with 1.6 and fused with 1.9 amperes. But immersed in water or any other liquid, it was so effectually cooled that the heaviest current at my disposal, rather more than 5 amperes, did not begin to raise it to redness. Twenty centimeters of this wire were coiled closely around a copper wire scarcely over 1 mm. in diameter, and the spring thus obtained, between 1.5 and 2 centimeters long, had all the stiffness needed and could be bent about to a considerable extent without causing the individual rings to come in contact with each other. In connecting this spiral the free ends were either wrapped round the hooks several times or were sealed directly into the mercury tubes, thus doing away with the heavier platinum wires. Both plans gave satisfactory contacts.[1]

Some care must be taken in so adjusting the spiral at the bottom as not to leave any great length of wire in a perpendicular position. It happened once or twice that vapor forming below rose in such a way as to protect a part of the wire above from actual contact with the liquid, and the part thus protected grew red-hot. Furthermore, caution must be used in putting the apparatus together not to let the bulb of the thermometer touch the sides of the vessel or either mercury tube. If it does, fluctuations in the readings will be observed.

A battery jar, filled with felt, but with a hole left in the middle just big enough for the boiling vessel, was pushed up over the whole apparatus after everything else was in place. This is a simpler and more effective insulation from drafts and from losses of heat by radiation than Beckmann's outer mantle containing boiling solvent. It has this disadvantage, that the boiling cannot be watched. On the other hand, it is not necessary to watch it where the constancy of the heating is so readily observed from the amperemeter, and the behavior of the thermometer gives all the information needed as to when an added portion of substance has dissolved, rising steadily to a point where it remains constant. If it is imperative to look inside, the jar of felt is easily let down, and a short time suffices to establish the former temperature when it is replaced. A Dewar vacuum-jacketed vessel would make an ideal apparatus for this method, offering as perfect insulation as could be desired, and at the same time transparency. Unfortunately, one could not be obtained at the time of carrying out these experiments.

Any constant source of electricity may be used, but for my purpose it was convenient to insert the apparatus in the dynamo circuit in series with the incandescent lamps. With 20 centimeters of 0.1 mm. diameter platinum wire and a current of about 1.8 amperes, the heat was sufficient to boil 30 cc. of water in five minutes. A coil of 10 centimeters of the wire and a current from 3 cells of a storage battery gave excellent results with low-boiling solvents.

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[1] The diameter of a spiral of such wire must be small. The first coils were wound over a stirring rod, but they were far too flexible, and neighboring rings could not be prevented from touching each other, thus cutting out a large part of the resistance. The wire was also wound around a glass rod and sealed on permanently. Loops were made at the ends and hung on the hooks, but when boiling began the whole coil was tossed about, making and breaking contact, so that with a high potential current sparking occurred, and the wire sometimes fused.

It is, perhaps, not the least of the advantages derived from the use of electricity, that the apparatus is so much simpler and less expensive than that now in use. Indeed, it may be put together in a short time from materials at hand in any laboratory.

The process of carrying out an experiment is in every respect identical with Beckmann's method, and need not be entered into. The first experiments had as their object to determine the constancy of the boiling-points obtained with pure solvents.

Experiment I, with Distilled Water.

Time in minutes.	Reading of thermometer.	Barometer.	Amperes.	True boiling-point of water under the observed pressure.[1]
4	water boiling	738.5	1.88	....
9	0.842	738.5	1.87	99°.201
19	0.850	....	1.86	....
40	0.854	....	...	....
44	0.856	738.7	1.87	99°.209
49	0.857	....	...	....
88	0.860	....	...	....
90	0.864	739.0	1.87	99°.220
92	0.863	....	...	....
95	0.863	....	...	....
97	0.862	739.0	...	....

The readings are not constant, but neither is the atmospheric pressure. The last column shows that the boiling-point of water rises 0°.019 when the pressure rises from 738.5 to 739.0 mm. If we assume that the water reached its true boiling-point some time between nine and nineteen minutes, say at a thermometer-reading close to 0.845, the increased pressure will account for the rise in the boiling-point to 0.864. As the amperemeter varied very little it was often left out in later experiments. It was not absolutely stationary, the needle oscillating slightly between limits of + or —0.01 amperes.

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[1] Landolt and Börnstein: Phys. Chem. Tabellen, p. 60.

Experiment II, with another Sample of Distilled Water.

Time in minutes.	Reading of thermometer.	Barometer.
10	0.790	736.6
20	0.790	736.6
22	0.792	....
25	0.790	....
30	0.789	....
40	0.792	736.6
87	0.792	736.5

The atmospheric pressure did not vary and the constancy of the thermometer readings is all that could be desired.

The rule was adopted in future experiments that to obtain the starting-point, or boiling-point of the pure solvent, the thermometer readings must not vary more than 0°.002 for fifteen minutes before the first portion of the substance is added. Ethyl alcohol, chloroform, and benzene were used as solvents, and there was never any difficulty in fulfilling these conditions when the atmospheric pressure did not change. Usually half an hour, sometimes three-quarters of an hour, elapsed before the first addition of substance.

Beckmann has measured the lowering effect on the boiling-point when glass beads are put in his apparatus.[1] In one of his experiments the addition of 13 grams of the beads lowered the boiling-point from 0°.60 to 0°.24, and they are an essential feature of his method to diminish superheating and bumping, as well as to favor a thorough uniformity of temperature in the boiling liquid. It does not seem possible for superheating to take place to any extent with my modification for reasons already stated, but the beads might help in securing uniformity of temperature. The experiment was tried with benzene as the solvent. The boiling-point was determined, first without, and then after successive additions of beads.

Experiment III, Effect of Beads.

Grams of beads.	Reading of thermometer.
0	1.805
3	1.795
13	1.779
23	1.765

[1] Ztschr. phys. Chem., **21**, 239.

An effect is here noticeable, but as it amounts to only 0°.040, in no way comparable to the difference of 0°.36 observed by Beckmann, it is safe to conclude that, while glass beads might be a slight advantage, they are by no means necessary. This is fortunate, for the coil, buried beneath the beads which hindered the free circulation of the liquid, often grew red-hot and several times fused.

A number of molecular weight determinations have been made, and the following examples will suffice to show the nature of the results :

Table I.

Solvent, ethyl alcohol. K = 11°.5.
Substance, naphthalene. Mol. wt., 128.

					Beckmann.[1]	
Grams solvent.	Grams substance.	Observed raising.	Grams substance in 100 grams solvent.	Molecular weight.	Grams substance in 100 grams solvent.	Molecular weight.
27.0895	0.1601	0.084	0.592	80.9		
	0.4945	0.203	1.82	103.4	2.42	148
	0.8670	0.322	3.20	114.3	4.14	155
	1.1903	0.431	4.39	117.2		
	1.6637	0.572	6.141	123.5		
	2.0920	0.692	7.722	128.3		
	2.5622	0.822	9.458	132.3		
	3.1927	0.984	11.78	137.8		

Table II.

Solvent, ethyl alcohol. K = 11°.5.
Substance, benzoic acid. Mol. wt., 122.

					Beckmann.[1]	
Grams solvent.	Grams substance.	Observed raising.	Grams substance in 100 grams solvent.	Molecular weight.	Grams substance in 100 grams solvent.	Molecular weight.
28.3919	0.3375	0.188	1.18	72.7	1.98	115
	0.5981	0.286	2.11	84.7		
	0.8885	0.396	3.13	90.9	3.04	121
	1.2469	0.535	4.39	94.4	4.42	124
	1.7926	0.746	6.31	97.3		
	2.4254	0.966	8.54	101.7		
	3.3989	1.297	11.97	106.1		

[1] Ztschr. phys. Chem., 6, 437.

Table III.

Solvent, ethyl alcohol. K = 11°.5.
Substance, salicylic acid. Mol. wt., 138.

					Beckmann.[1]	
Grams solvent.	Grams substance.	Observed raising.	Grams substance in 100 grams solvent.	Molecular weight.	Grams substance in 100 grams solvent.	Molecular weight.
30.0900	0.1695	0.091	0.563	71.2	1.37	129
	0.4240	0.182	1.41	89.0		
	0.7890	0.300	2.62	100.5		
	1.2170	0.431	4.04	107.9	2.76	139
	1.8589	0.627	6.18	113.3	5.29	140
	2.5876	0.850	8.60	116.3	8.91	142
	3.5757	1.157	11.88	118.1		
	5.0180	1.611	16.68	119.0	13.40	142
	6.5996	2.121	21.93	118.9	17.29	143

Table IV.

Solvent, chloroform. K = 36°.6.
Substance, benzoic acid. Mol. wt., 122.

					Beckmann.[1]	
Grams solvent.	Grams substance.	Observed raising.	Grams substance in 100 grams solvent.	Molecular weight.	Grams substance in 100 grams solvent.	Molecular weight.
52.3229	0.1659	0.139	0.317	83.5	0.85	199
	0.6051	0.360	1.16	117.6	1.73	208
	1.3742	0.673	2.63	142.8	3.44	219
	2.1692	0.980	4.15	154.8	5.15	220
	3.2744	1.379	6.258	166.1		
	4.3140	1.733	8.245	174.1	8.61	226
	5.7073	2.210	10.91	180.6		

These results are uniformly lower than those obtained by Beckmann with the same solvents and substances, as may be seen by comparing his figures, contained in the last two columns, with mine. This is possibly due to the fact that no great pains were taken to purify the solvents, the object not being to duplicate Beckmann's results, but to demonstrate the usefulness of this modification of the boiling-point method. And the regularity of the results demonstrates this sufficiently.

Electric heating is not adapted for use with water solutions, for difficulties due to electrolysis would surely be encountered. This is no serious limitation, for owing to its very small molecular raising of the boiling-point and its strong dissociating effect, water would never be selected if another solvent could be used. It was feared that complications might arise with other solvents owing to the action of the current. In fact the remarkably low results, obtained with very dilute solutions, seem to point to a form of dissociation, under the conditions of the experiment, of non-electrolytes in solvents to which it is not usual to ascribe a dissociating power. It is my purpose to continue the investigation with a large number of solvents and substances and varying currents to learn more concerning this interesting phenomenon.

The best test of a new method is in its application. Fourteen students were carrying out determinations by the boiling-point method for the first time. Eight used the old form of apparatus and six electric heating. The results obtained by the six were without exception better than those obtained by the eight.

LABORATORY OF PHYSICAL CHEMISTRY,
ANN ARBOR, MICHIGAN, June, 1899.

A CONTRIBUTION TO OUR KNOWLEDGE OF DICARBONYL CUPROUS CHLORIDE.

BY WILLIAM APP JONES.[1]

INTRODUCTION.

In attempting to determine the free oxygen in illuminating gas by means of an ammoniacal solution of cuprous chloride, Leblanc, Stas, and Doyère[2] observed that a large quantity of carbon monoxide and ethylene were also absorbed.

Leblanc then showed that carbon monoxide is absorbed by a hydrochloric acid solution of cuprous chloride, easily and with only a very slight rise in temperature, and the same was found true for an ammoniacal solution. He believed that in both cases the proportion of carbon monoxide to cuprous chloride was 1 : 1.

Leblanc also noticed that by an elevation of temperature or

[1] The work, an account of which is here given, was undertaken at the suggestion of Professor Remsen and carried out under his guidance. The article formed the dissertation submitted by the author to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1898.

[2] Compt. rend. (1850), 30, 483.

by a removal of the atmospheric pressure from these solutions the carbon monoxide was given off as such, and that ammoniacal solutions of the cuprous salts in general have the power to absorb this gas. He did not succeed in isolating any definite compounds from these solutions.

In 1856 Berthelot[1] succeeded in isolating the compound formed by passing carbon monoxide through a cold saturated solution of cuprous chloride in concentrated hydrochloric acid. He obtained beautiful pearly plates which altered very rapidly in the air, making it impossible to prepare them for analysis without at least some loss of carbon monoxide. The figures obtained by his analyses approximated those required by the formula $4Cu_2Cl_2.3CO.7H_2O$, but since the compound alters so rapidly he believed it to be $Cu_2Cl_2.CO.2H_2O$. Evidently this formula is based upon very unsatisfactory evidence, and the present work was undertaken to determine more accurately, if possible, the composition of the substance, to study its conduct under different conditions of temperature and pressure, and to determine the chemical activity of the carbon monoxide at the moment of its liberation.

PREPARATION OF MATERIAL.

Cuprous Chloride.

This was prepared by the action of *aqua regia* on copper turnings—the latter being in excess. In its preparation about half a liter of concentrated hydrochloric acid was poured into a flask containing 300–350 grams of the copper turnings, and the acid heated almost to boiling. Small quantities of concentrated nitric acid were then introduced from time to time and the heating continued for half an hour, when the hot solution was quickly filtered through asbestos and the cuprous chloride precipitated in the form of a fine white powder by the addition of several liters of cold water. The precipitate was then filtered off quickly and washed from acid, the final washings being made with glacial acetic acid. The material was at once dried in an air-bath, at a temperature of 115°–125° C., for twelve hours. Proceeding in this way it is possible to obtain cuprous chloride perfectly dry and white, and a specimen kept for six months in a glass-stoppered bottle suffered no change in color. The analysis of the material gave the following results:

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[1] Ann. chim. phys. [3], 46, 488.

I. 0.2012 gram material gave 0.1607 gram CuO.

II. 0.2112 gram material gave 0.1692 gram CuO.

	Calculated for Cu_2Cl_2.	Found. I.	Found. II.
Cu	64.06	63.72	63.94

Preparation of Carbon Monoxide.

The carbon monoxide used in most of the experiments was prepared by the action of sulphuric acid on potassium ferrocyanide, though comparative experiments were made with carbon monoxide obtained by the action of sulphuric acid on formic acid. In both cases the gas was passed through four or five wash-bottles, containing a concentrated solution of caustic potash and, when all the air had been displaced, it was collected in a glass gasometer.

Preparation of Dicarbonyl Cuprous Chloride.

In preparing this compound the cuprous chloride was placed in a small balloon flask, which in turn was immersed in ice-water. The flask was tightly fitted with a three-hole rubber stopper; through one opening a small dropping funnel was passed, and through the others glass tubes, provided with stop-cocks and bent at right angles, one of which was connected with a gas burette, the other with a suction-pump. The dropping-funnel and the tube leading to the gas burette were closed, connection made with the pump, and the flask exhausted. The connection with the pump was closed and enough hydrochloric acid introduced through the dropping-funnel to form a thin paste with the cuprous chloride. The tube leading to the gas burette, which contained carbon monoxide, was then opened and the absorption flask alternately shaken and immersed in ice-water. The absorption, which is at first quite rapid, toward the end becomes very slow, and only after several hours is it complete; frequent shaking is absolutely necessary.

The absorption being complete, ice-water was added, and the crystals which separated were quickly filtered and washed with ice-water, and then pressed between sheets of drying-paper with a previously cooled spatula. Unless the washing and drying has been done *very* quickly the white plates will have become a green paste, and in any case there will be a slight alteration.

Analysis of the Compound.

Decomposition Method.—As shown above, it is impossible to dry and then weigh the compound for analysis. In the first instance the material was washed and dried as quickly and thoroughly as possible, and then decomposed by an elevation of temperature, the products being either measured or weighed.

The apparatus for the decomposition consisted of a small bulb of about 6 cc. capacity, into which the compound was introduced. This bulb was provided with a two-hole rubber stopper: through one opening was passed a small glass tube, bent at right angles, which extended to the bottom of the flask, and was connected with a calcium chloride tube. This was closed during the decomposition.

A similar glass tube was introduced through the other opening, which extended just below the stopper, and was connected with a weighed calcium chloride tube in which the water given off by the decomposition of the compound was collected. This tube was protected by another calcium chloride tube, the latter being connected with a gas-measuring tube in which the carbon monoxide was to be collected. During the decompositions the little bulb containing the material was immersed to a given-point in a water-bath maintained at 80° C., and blank determinations were previously made to ascertain the correction to be applied to the volume of carbon monoxide collected, the correction being the expansion of the gas in the bulb.

The compound was prepared as previously described, dried very quickly between sheets of drying-paper, and at once transferred to the decomposition bulb, which had previously been weighed. The stopper was at once inserted and connection made with the weighed calcium chloride tube, the protecting calcium chloride tube, and the gas measuring tube. The decomposition bulb was placed in the water-bath, and a temperature of 80° C. maintained until there was no change in the volume of gas collected. This volume was corrected for temperature, pressure, water-vapor, and for the expansion of the gas in the decomposition-bulb. The volume of carbon monoxide having been ascertained, the measuring-tube was disconnected and dry carbon dioxide pressed through the calcium-chloride tube previously closed, and the tube leading to the bottom of the decomposition-flask. This was continued until there was no change in the weight of the weighed calcium-chloride tube, when a final weighing of this tube and the decomposition-bulb was made, giving respectively the weight of the water and cuprous chloride in the compound. From the volume of carbon monoxide collected, its weight was calculated.

While this method is theoretically very simple, it is in reality very difficult on account of the extreme instability of the compound, which makes it almost, if not quite, impossible to dry it without some decomposition. While the method is rather unsatisfactory in the results obtained, yet it was the only one by which it was possible to determine the amount of water present.

The results of three analyses are given on page 292.

Absorption Method.—This method was also employed, as the results obtained were found to be more accurate than those obtained by the former method. From 1 to 2 grams of cuprous chloride were carefully weighed and introduced into an absorption bulb, similar to that described on page 289. The bulb was then closed, immersed to the mark in ice-water, and exhausted. The exhaustion being complete, connection with the pump was closed, enough concentrated hydrochloric acid introduced to form a thin paste with the cuprous chloride, the connection with the gas tube opened, and carbon monoxide allowed to enter, and the volume of gas in the measuring tube was quickly noted as soon as atmospheric pressure was reached in the absorption bulb. The bulb was then alternately shaken and immersed in ice-water until absorption was complete. This required about three hours, and toward the end of this time the flask must be shaken almost con-

	I.		II.		III.	
Cu_2Cl_2	0.3280 gram	= 60.78 per cent	0.2180 gram	= 62.21 per cent	0.2170 gram	= 62.41 per cent
H_2O	0.1220 ‘‘	= 22.61 ‘‘	0.0740 ‘‘	= 21.11 ‘‘	0.0750 ‘‘	= 21.57 ‘‘
CO	0.0896 ‘‘	= 16.60 ‘‘	0.0584 ‘‘	= 16.67 ‘‘	0.0557 ‘‘	= 16.02 ‘‘
Total	0.5396 ‘‘	= 99.99 ‘‘	0.3504 ‘‘	= 99.99 ‘‘	0.3477 ‘‘	= 100.00 ‘‘

Same results calculated in terms of Cu_2Cl_2 and CO for comparison with those recorded on page 293.

	I.		II.		III.	
Cu_2Cl_2	0.3280 gram	= 78.54 per cent	0.2180 gram	= 78.87 per cent	0.2170 gram	= 79.57 per cent
CO	0.0896 ‘‘	= 21.45 ‘‘	0.0584 ‘‘	= 21.13 ‘‘	0.0557 ‘‘	= 20.42 ‘‘
Total	0.4176 ‘‘	= 99.99 ‘‘	0.2764 ‘‘	= 100.00 ‘‘	0.2727 ‘‘	= 99.99 ‘‘

stantly. In some instances the bulb was kept in ice-water for several days, being shaken at intervals, but no gas was absorbed after the first three hours, when this part of the operation had received the proper treatment.

Determinations were also made to see if the strength of acid used had any influence on the amount of carbon monoxide absorbed. It was found to have no effect, except that the absorption was the more rapid the more concentrated the acid used. This fact is doubtless due to the greater solubility of both compounds in the stronger acid.

These results led me to try pure water, and, while the absorption is very slow, exactly the same amount of carbon monoxide is absorbed as when hydrochloric acid is used.

When the bulb containing dicarbonyl cuprous chloride is heated to 60° or 70° C., exactly the same amount of carbon monoxide is given off as was originally absorbed. On cooling the bulb it is exactly reabsorbed, and this operation can seemingly be repeated indefinitely. Dry cuprous chloride does not absorb dry carbon monoxide.

I give below four analyses in the order in which they were made :

	Weight Cu_2Cl_2.	Weight CO absorbed.	Per cent CO.	Remarks.
IV.	2.0006	0.5437	21.37	Cu_2Cl_2 in water
V.	1.0045	0.2703	21.20	Cu_2Cl_2 in 1HCl : $4H_2O$
VI.	1.0069	0.2733	21.35	Cu_2Cl_2 in 1HCl : $2H_2O$
VII.	1.0027	0.2749	21.51	Cu_2Cl_2 in conc. HCl.

I am aware that there is one considerable source of error in this method. The compound formed, as well as the cuprous chloride, is insoluble in water, and only slightly soluble in hydrochloric acid, so that no matter how long the absorption is continued nor how vigorously the bulb is shaken, some unchanged cuprous chloride will always be enclosed in the compound formed, causing the percentage of gas absorbed to be slightly low. The percentage of carbon monoxide required by different formulas is as follows :

$Cu_2Cl_2.CO$ requires $CO = 12.41$
$4Cu_2Cl_2.7CO$ " $CO = 19.91$
$5Cu_2Cl_2.9CO$ " $CO = 20.37$
$6Cu_2Cl_2.11CO$ " $CO = 20.66$
$12Cu_2Cl_2.23CO$ " $CO = 21.40$
$Cu_2Cl_2.2CO$ " $CO = 22.13$

It is evident that the formulas considered probable by Leblanc ($Cu_2Cl_2.CO$) and the one assigned to the compound by Berthelot ($Cu_2Cl_2.CO.2H_2O$) cannot be entertained. The percentage of carbon monoxide in $Cu_2Cl_2.CO$ is only 12.41; the average of more than fifty determinations made by me, and varying from one another by only a few tenths of a per cent, is about 21.4 per cent.

Exactly 21.4 per cent of carbon monoxide is removed by the formula $12Cu_2Cl_2.23CO$. While such complex compounds are not unknown in inorganic chemistry, certainly they are quite rare, and while the percentage of carbon monoxide required by $Cu_2Cl_2.2CO$ is 22.13, yet there is a constant error in both methods, causing the results to be slightly low, so that it seems to me fair to accept the formula $Cu_2Cl_2.2CO$ as highly probable.[1]

As regards the proportion of water present, we must rely entirely on the decomposition method. While this was found to be not as accurate as could be desired, yet there is a certain rough agreement. In three successive determinations the percentages of carbon monoxide found were 21.45, 21.13, and 20.42. These results show that the compound had slightly decomposed in drying, yet the average percentage of carbon monoxide (21.0) is only slightly below the average obtained by the other method (21.4). Keeping the proportions $Cu_2Cl_2.2CO$ constant and varying the proportion of water, we obtain:

$Cu_2Cl_2.2CO.3H_2O$ contains $H_2O = 17.55$ per cent.
$Cu_2Cl_2.2CO.4H_2O$ " $H_2O = 22.11$ "
$Cu_2Cl_2.2CO.5H_2O$ " $H_2O = 26.19$ "

The average percentage of water was found to be 21.76 (page 292), only 0.35 per cent lower than required by $Cu_2Cl_2.2CO.4H_2O$. On the other hand it is 4.21 per cent higher than required by $Cu_2Cl_2.2CO.3H_2O$ and 4.43 per cent lower than required by $Cu_2Cl_2.2CO.5H_2O$. This makes it seem highly probable that the composition of dicarbonyl cuprous chloride is expressed by the formula $Cu_2Cl_2.2CO.4H_2O$.

Behavior of Dicarbonyl Cuprous Chloride under Reduced Pressure.

Leblanc pointed out that this compound loses carbon monoxide when the atmospheric pressure is removed, yet no exact statement has been made in regard to this point, so experiments were undertaken with this object in view.

The compound was prepared in a bulb of 5 cc. capacity. This bulb was provided with a dropping-funnel having a three-way stop-cock, so that it could be disconnected or connected with a gas measuring tube containing carbon monoxide, and with a Sprengel pump. A manometer was connected with the tube leading to the pump. Blank experiments were made to ascertain the correction, due to the expansion of the air in the bulb and tubes. For this purpose the bulb, containing the same amount of water as that used in the actual experiments, was immersed to the mark in ice-water, and the pump started. The gas pumped out at different pressures was collected in a measuring tube and corrected for temperature, pressure, and water vapor. These corrections are:

Pressure. mm.	Vol. air collected. cc.	Pressure. mm.	Vol. air collected. cc.
460	29.9	130	60.0
360	39.0	100	63.2
260	48.2	60	66.4
160	57.6	40	68.0

The compound having been prepared in the usual manner, it was only necessary to close the connection with the gas burette and open the stop-cock leading to the pump.

The first series, in which dilute acid was used, is as follows:

Table I.

0.5058 gram Cu_2Cl_2 (in 1HCl : $12H_2O$) absorbed 0.1364 gram (109 cc.) Co (= 21.24 per cent).

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	29.99	29.9	0.09	0.07
360	39.40	39.0	0.40	0.35
260	49.20	48.2	1.00	0.87
160	59.80	57.6	2.20	1.92
135	170.16	59.3	111.86	98.12
40	182.01	68.0	114.01	100.00

At each pressure given above the pump was stopped for twenty-four hours to see that the reading was constant, and at the end of a week, at a pressure of 160 mm., only 2.2 cc. of gas had been given off. When the pressure was lowered to 135 mm. bubbles of gas were given off rapidly, and at the end of nine days more 111.86 cc. of gas had been given off. When a constant reading had been obtained the pressure was lowered to 40 mm. and this maintained for a week, but only 2.15 cc. of gas were given off in this time.

Table II.

0.4910 gram Cu_2Cl_2 (in 1 HCl : 12H_2O) absorbed 0.1319 gram (105.5 cc.) CO (= 21.17 per cent).

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	30.2	29.9	0.3	0.28
360	39.4	39.0	0.4	0.37
260	49.5	48.2	1.3	1.21
160	59.6	57.6	2.0	1.87
135–125	165.6	59.3	106.3	99.42
40	274.9	68.0	106.9	100.00

These two decompositions are given as extremes, the first being exceptionally poor, the last slightly better than the average. In all cases slightly more gas was collected than originally absorbed. It was impossible to dispense with all rubber connections, and although these were kept well covered with shellac, one could hardly expect to prevent diffusion of air into the apparatus when such a low pressure was maintained for three weeks. It seems, therefore, that the compound made in dilute hydrochloric acid is not decomposed until the pressure is reduced to 135–125 mm., and that it is completely decomposed at this point.

Behavior of the Compound Made with Water.

The compound obtained by the absorption of carbon monoxide by cuprous chloride in water, was next submitted to reduced pressure.

Table I.

Co absorbed = 90.05 cc.

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	30.1	29.9	0.2	0.22
360	39.3	39.0	0.3	0.33
260	49.0	48.2	0.8	0.88
160	58.8	57.6	1.2	1.32
130	102.7	60.0	42.7	46.97
100	109.2	63.2	45.7	50.27
60	156.9	66.4	90.5	99.55
40	158.9	68.0	90.9	100.00

By way of explanation, it should be stated that in lowering the pressure from 760–160 mm. only 1.2 cc. of carbon monoxide were given off, but at 130 mm. the evolution of gas increased, and at the end of five days 42.7 cc., or 2.32 cc. less than half the amount absorbed, had been collected when the reading became constant. In lowering the pressure from 130–60 mm. only about 5 cc. of gas were given off, but at 60 mm. the evolution again increased and continued until the compound was decomposed.

Table II.

CO absorbed = 103.33 cc.

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	30.2	29.9	0.3	0.28
360	39.4	39.0	0.4	0.37
260	49.2	48.2	1.0	0.95
160	59.0	57.6	1.4	1.33
130	109.99	60.0	49.99	47.70
100	114.92	63.2	51.72	49.35
60	170.89	66.4	104.49	99.63
40	172.87	68.0	104.87	100.00

	cc.
Total vol. gas collected	104.87
" " " absorbed	103.33
Difference	1.54

	cc.
One-half vol. gas absorbed	51.66
Vol. gas given off at 130 mm.	49.99
Difference	1.67

It was noticed in these decompositions that a dark coating was formed in the bulb, having a metallic appearance when deposited slowly and in fine condition. This coating gave the copper test distinctly. The fact will be referred to later.

Behavior of the Compound made with Concentrated Hydrochloric Acid.

The results of one determination will show this behavior in a general way.

CO absorbed = 105.2 cc.

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
410	40.7	39.2	1.5	1.38
310	60.2	44.7	15.5	14.32
260	74.4	48.2	26.2	24.21
210	91.8	52.9	38.9	36.95
160	117.2	57.6	59.6	55.08
130	168.2	60.0	108.2	100.00

It will be seen from the above that in this instance decomposition begins at about 410 mm. pressure and gradually increases to 160 mm., when it increases more markedly until decomposition is complete at 130 mm.

This decomposition agrees with those in which dilute acid was used in that decomposition is complete at 130 mm.; it differs from both in that marked decomposition begins below 130 mm. The stronger the acid the greater the ease with which carbon monoxide is absorbed, and also giving off again under reduced pressure. These results are discussed and the decompositions expressed in the form of curves on page 310.

Absorption of Carbon Monoxide by Cuprous Chloride in Pyridine.

It was desired to test the effect of increased temperature on some compound of cuprous chloride and carbon monoxide. The compound made with water or hydrochloric acid is too sensitive to heat to be studied with accuracy. W. Lang[1] has noted that cuprous chloride in pyridine has the power to absorb carbon monoxide ; this compound was prepared and found to have the stability desired.

The method of preparation was similar to that described on page 289. No matter how carefully the bulb was exhausted, the instant the pyridine came in contact with the cuprous chloride, both assumed a deep-green color and the bulb became slightly warm. The material showed an annoying tendency to form small hard lumps, and it was necessary to heat to 60° or 70° C. to get these lumps broken and into solution. Complete solution was doubtful even then, as the liquid was so dark that it was impossible to see through it.

Having obtained a solution as nearly perfect as possible, the absorption of carbon monoxide was effected as in the former experiments. The compound formed appeared as shining white plates on the bottom of the bulb and, on the addition of ice-water, more of the material was precipitated. All attempts to filter and dry this compound failed, as the crystals instantly turn green in the air.

As the compound formed by the absorption of carbon monoxide by cuprous chloride in pyridine is too unstable to admit of drying it, recourse must be had to the absorption method. A large number of determinations were made, and below is given a series showing the extremes. The average tended rather to the higher than the lower percentage.

Weight Cu_2Cl_2.	Weight CO absorbed.	Per cent CO.
1.0005	0.172637	14.71
0.2020	0.035630	14.98
0.2055	0.036319	15.00
0.4036	0.072710	15.26
0.4028	0.076182	15.90
0.2040	0.039030	16.05

It will be seen at once that the results vary quite widely, probably in consequence of the caking of the cuprous chloride, thereby making absorption incomplete. If the relation of cuprous chloride to carbon monoxide is a simple one, it is probably represented by the formula $2Cu_2Cl_2.3CO$, since the percentage of carbon monoxide, as determined, is undoubtedly low.

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[1] Ber. d. chem. Ges., 21, 1584.

The percentages required by the simpler hypothetical compounds are the following :

$Cu_2Cl_2.CO$ requires $CO = 12.41$
$2Cu_2Cl_2.3CO$ " $CO = 17.57$
$3Cu_2Cl_2.5CO$ " $CO = 19.15$
$Cu_2Cl_2.2CO$ " $CO = 22.13$

Behavior of the Compound under Increased Temperature.

The method of work was the following : Into a bulb of 25 cc. capacity a weighed quantity of cuprous chloride (about 0.403 gram) was introduced and the bulb closed with a two-hole rubber stopper. Through one opening was passed a dropping funnel and through the other a bent glass tube. The bulb was then exhausted and nitrogen allowed to enter until all air had been displaced, 5 cc. of pyridine introduced, connection made with a gas burette, and the bulb immersed to a given mark in a water-bath, the temperature of which was accurately regulated. As the temperature of the bath was raised, the gas expelled on account of expansion was collected and, at the desired points, the temperature was kept constant for an hour, when final readings were made. The corrections used in the determinations were as follows :

Temperature of bath.	Vol. gas collected. cc.	Temperature of bath.	Vol. gas collected. cc.
0°	0.000	60°	8.592
10°	1.869	70°	10.863
20°	2.849	80°	13.578
30°	3.917	90°	16.739
40°	5.164	100°	21.401
50°	6.767		

In the actual experiments it was always impossible to get off as much gas as was originally absorbed. This may have been influenced by a difference in the vapor-tension of the liquid in the blank and real determinations, or to a reaction between the pyridine and rubber connections, or between the pyridine and cuprous chloride. After each determination the bulb contained a coating of what seemed to be metallic copper, but more abundant than that mentioned previously (page

298). It is conceivable that this reaction had taken place to a slight extent:

$$Cu_2Cl_2 + CO \longrightarrow 2Cu + COCl_2,$$

and then $$COCl_2 + H_2O \longrightarrow 2HCl + CO_2.$$

If carbon dioxide was formed it was, of course, dissolved by the water in the gas burette, making the readings low.

In the experiments the compound was prepared as previously described, and the decompositions made as in the blank determinations.

Table I.

0.4036 gram Cu_2Cl_2 absorbed 0.0727 gram (= 58.144 cc. CO)CO (= 15.26 per cent).

Temperature.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
10°	2.717	1.869	0.848	1.45
20°	13.858	2.849	11.009	18.93
30°	22.283	3.917	18.366	31.58
40°	31.188	5.164	26.024	44.75
50°	40.012	6.767	33.245	57.17
60°	47.565	8.592	38.973	67.02
70°	54.571	10.863	43.708	75.17
80°	61.207	13.578	47.629	81.90
90°	68.824	16.739	52.085	89.57
100°	76.029	21.401	54.628	93.95

Table II.

0.4042 gram Cu_2Cl_2 absorbed 0.0702 gram (= 56.16 cc. CO) CO (= 14.79 per cent).

Temperature.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
10°	4.016	1.869	2.147	3.82
20°	11.849	2.849	9.000	16.02
30°	23.138	3.917	19.221	34.22
40°	28.158	5.164	22.994	40.94
50°	39.015	6.767	32.248	57.42
60°	47.934	8.592	39.342	70.05
70°	53.951	10.863	43.088	76.72
80°	61.831	13.578	48.253	85.92
90°	68.042	16.739	51.303	91.35
100°	74.595	21.401	53.194	94.71

These results are expressed in the form of curves on page 310.

Action of Oxygen on Dicarbonyl Cuprous Chloride.

These experiments were undertaken to determine whether or not the carbon monoxide possess unusual activity at the moment of liberation from the compound. When oxygen, free from carbon dioxide, is passed through dicarbonyl cuprous chloride, even at 0°, the compound instantly turns green, and the gaseous mixture when conducted through baryta water, shows the presence of carbon dioxide. The cuprous chloride contained no material which could give carbon dioxide, for, when oxygen was conducted through this material, suspended in water, and then through baryta water for several hours, not the least precipitate was formed.

Thinking that carbon monoxide might be alternately absorbed and given off, when a mixture of this gas and oxygen is allowed to pass through moist cuprous chloride at 0°, the following method of work was adopted: From 1 to 2 grams of cuprous chloride were placed in a flask and covered with water. This flask was provided with a two-hole rubber stopper, through each opening of which was passed a glass tube bent at right angles, one reaching just below the stopper and the other to the bottom of the flask. The stopper and tubes being in place, the flask was connected with a series of wash-bottles, so that the current of gas used passed first through two wash-bottles containing caustic soda, then through a baryta solution into the cuprous chloride. On issuing from this flask it passed through another bottle containing baryta water, which was protected from the air by a bottle containing a solution of caustic soda. At first pure oxygen was passed through this series for about two hours. The cuprous chloride became slightly green, and neither the baryta solution before or beyond the cuprous chloride flask showed any signs of cloudiness. Without disturbing the apparatus, carbon monoxide was mixed with the oxygen and, when the mixture had been passed for fifteen minutes, a coating began to appear on the entrance tube of the baryta bottle beyond the cuprous chloride flask. At the end of two hours a perceptible precipitate had been formed, while the baryta solution before the cuprous chloride flask remained entirely clear. A determination of the barium carbonate showed that the carbon dioxide formed was less than 1 per cent of the carbon monoxide employed. This experiment was repeated several times, and always with the same result.

The passage of a mixture of oxygen and carbon monoxide over ferrous sulphate or chloride does not cause the formation of carbon dioxide.

Action of Chlorine on Dicarbonyl Cuprous Chloride.

If carbon monoxide possesses unusual activity at the moment of liberation from this compound, we should expect it to show this quite markedly in its conduct toward chlorine. If carbonyl chloride should be formed it would react with the water of crystallization in the compound.

The apparatus consisted of a flask for the preparation of the compound, which was provided with an inlet tube reaching to the bottom, and an outlet tube extending just below the stopper. The outlet tube was connected with a larger tube containing finely powdered antimony, which was in turn connected with a gas measuring tube containing caustic potash. In the preparation of the compound a flask of known size was employed, and the amount of carbon monoxide absorbed was accurately measured. The flask containing the compound was then connected with the antimony tube, and also with a chlorine generator, from which the air had been expelled as completely as possible. When the inlet tube, containing chlorine, was opened, the tube leading from the absorption flask and connected with the antimony tube and gas measuring tube was also opened. The moment the chlorine touched the crystals of dicarbonyl cuprous chloride they turned green and gave off bubbles of gas. The passage of chlorine was continued until all the material had gone into solution, showing complete oxidation of the cuprous chloride. The excess of chlorine was taken up by the antimony and any carbon dioxide formed was absorbed by the caustic soda, while the unchanged carbon monoxide was collected.

At the end of the operation the vessel originally containing the dicarbonyl cuprous chlorine was filled with water, so as to drive over all the gas contained in it. Knowing the amount of carbon monoxide absorbed, as well as the capacity of the absorption bulb, and hence the volume of free carbon monoxide contained in it after absorption, it was only necessary to subtract the volume of gas collected from the sum of these two to determine the amount of carbon monoxide that had been changed. Blank experiments showed that powdered antimony has not the power of effecting union between carbon monoxide and chlorine. All experiments were performed in diffused daylight.

The rate of flow of the chlorine seemed to affect the amount of carbon dioxide changed, this being greater the slower the current. The same effect was produced by lowering the temperature, thus retarding the decomposition of the compound. For these reasons it was impossible to get entirely concordant results. Below I give an average series of determinations:

CO absorbed. cc.	CO collected. cc.	CO changed. cc.	Per cent changed.
63.2	62.4	0.8	1.26
54.1	52.0	2.1	3.88
69.0	68.4	0.6	0.86
78.6	76.6	2.0	2.54
77.2	73.1	4.1	5.31

From these results it seems that there is a slight reaction between the two gases, but if the carbon monoxide possesses unusual activity, we should expect a greater change than the above figures indicate.

Action of Hydrogen on Dicarbonyl Cuprous Chloride.

Since oxygen has the power to decompose this compound even at and below 0°, it seemed advisable to try the action of hydrogen. The compound was prepared in the usual manner, and the bulb containing it, still immersed in ice-water, was introduced into a system of gas wash-bottles, similar to that described on page 302. Hydrogen, prepared by the action of hydrochloric acid on pure zinc, and then washed with caustic potash, lead acetate, and potassium permanganate, was passed through the compound for eight hours. At the end of this time the crystals had in no way changed their appearance, and the water contained in the wash-bottles, through which the gas passed on leaving the flask containing the compound, had neither taste nor odor, was neutral in reaction, and did not reduce Tollens' solution in the cold. The compound was then allowed to assume the room temperature, and finally decomposed by warming to 60°, but no change in the carbon monoxide could be detected.

Action of Nitrogen.

These experiments were conducted exactly as in the case of hydrogen. At 0° the compound was not affected by nitrogen, and when the bulb was warmed so as to drive off the carbon monoxide no change whatever could be detected in the latter.

DISCUSSION OF RESULTS.

Action of Oxygen on Dicarbonyl Cuprous Chloride.

There can be no doubt that when oxygen is passed into this compound at 0° it undergoes decomposition, and there is formed simultaneously a small amount of carbon dioxide. This carbon dioxide cannot be due to an impurity in the cuprous chloride, for oxygen passed through the same material gives us no carbon dioxide whatever. Neither can it be due to a peculiar activity of the oxygen brought about by the cuprous chloride through its oxidation, thus causing a splitting of the molecular into atomic or active oxygen, for, when a mixture of oxygen and carbon monoxide is passed through ferrous sulphate or chloride these compounds are oxidized, yet no carbon dioxide is formed. The oxidation of carbon monoxide by the action of oxygen on dicarbonyl cuprous chloride must be due to the activity of the carbon monoxide, or else it is brought about through the agency of the cuprous chloride.

While we have some evidence pointing to the fact that both elements and compounds are unusually active at the moment of their liberation, yet it is far from certain that this activity is a property of the element or compound *per se*. Both heat and electrical phenomena are possibly involved, so that at present we have no satisfactory explanation of the real or apparent activity of the nascent state. If the formation of carbon dioxide is due to the activity of the carbon monoxide, it is surprising that this activity is not expressed more strongly toward chlorine.

Drehschmidt has shown[1] that when an ammoniacal solution of cuprous chloride is used for the absorption of carbon monoxide, metallic copper is formed, this being due, as he thinks, to a reduction of the cuprous chloride by the carbon monoxide.

Winkler[2] shows that caustic potash causes the precipitation of metallic copper from a solution of cuprous chloride containing carbon monoxide; carbon dioxide is formed at the same time.

Winkler also points out[3] that by the action of carbon monoxide on a solution of cuprous chloride and palladium chloride, palladium is precipitated and carbon dioxide formed, thus: $PdCl_2 + CO + H_2O = Pd + CO_2 + 2HCl$. In the absence of cuprous chloride this reaction takes place much more slowly.

As previously stated, in the decomposition of dicarbonyl cuprous chloride by reduced pressure, as well as in the decomposition of the pyridine compound by an elevation of temperature, a coating was formed which had the appearance of metallic copper and gave the test for copper. Considering these facts it seems probable that the formation of carbon dioxide is due to this reaction:

$$Cu_2Cl_2 + CO + H_2O = 2Cu + CO_2 + 2HCl.$$

The Constitution and Chemical Nature of Dicarbonyl Cuprous Chloride.

As regards the structure of this compound I have no suggestion to offer. Formulas might be written to satisfy all the bonds of the elements involved, but there is no experimental basis for such a procedure. It seems fairly certain that its composition is represented by the formula $Cu_2Cl_2.2CO.4H_2O$. Remembering that both cuprous chloride and carbon monoxide are unsaturated compounds, it does not appear unnatural that they should unite and mutually saturate each other. How the parts are united is a far more difficult question.

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[1] Ber. d. chem. Ges., **20**, 2754.

[2] Ztschr. anal. Chem., **28**, 272.

[3] *Loc. cit.*, 274.

What is more important, and regarding which there is some strong evidence, is a consideration whether the compound is in reality a true chemical individual, an "atomic," as opposed to "molecular," compound. The material has a constant crystal form and luster. It is quite stable at low temperatures in the absence of active substances. If the temperature is elevated or the pressure greatly reduced, it undergoes decomposition, but in a manner similar to compounds, the atomic nature of which is not doubted. In confirmation of this I cite the following cases:

Effect of Pressure Changes on the Molecular Weight of Compounds.

It was observed by Naumann[1] that not only does the density of acetic acid vary with the temperature but also with the pressure, temperature remaining constant.

Acetic Acid—Temperature 100°.

Pressure. mm.	Density.	Pressure. mm.	Density.
393	3.44	168	3.01
342	3.37	156	2.98
258	3.17	130	2.94
232	3.12	92	2.76
186	3.06	77	2.66

Theoretical for $C_2H_4O_2 = 2.073$
" " $C_4H_8O_4 = 4.150$

Similar results were obtained at temperatures ranging from 78°–185°, and the work confirmed by Ramsay and Young[2] through a much wider range of pressures.

The molecular weight of hydrofluoric acid as determined by Gore[3] corresponds to the formula HF. The molecular weight, as determined by Mallet,[4] at 30° C., is 39.32, almost exactly that required by H_2F_2. By a more extensive investigation Thorpe and Hambly[5] have shown that, at the ordinary temperature, the compound is to be expressed by the formula HF. On lowering the temperature the molecule becomes more complex and finally approaches H_3F_3. The change in density is gradual, there being no sharp breaks, as this series of determinations shows.

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[1] Ann. Chem. (Liebig), **155**, 325.

[2] Jour. Chem. Soc., **49**, 790.

[3] *Ibid.*, **22**, 377.

[4] This Journal, **3**, 189.

[5] Jour. Chem. Soc., **53**, 765, and **55**, 163.

Temperature.	Partial pressure. mm.	Vapor-density (H = 1).	Corresponding molec. weight.
32.0°	743	19.87	39.74
32.2°	686	17.89	35.78
31.8°	655	16.99	33.98
32.0°	603	15.41	30.82
32.5°	545	13.89	27.78
32.3°	498	13.27	26.54
31.9°	354	11.50	23.00
32.3°	353	11.39	22.78

Naumann has proved[1] in the case of nitrogen peroxide that for a given temperature the dissociation of N_2O_4 into NO_2 is greater the less the pressure.

Temperature.	Pressure. mm.	Dissociated. Per cent.	Temperature.	Pressure. mm.	Dissociated. Per cent.
18.0°	279	17.3	20.0°	301	17.8
18.5°	136	29.8	20.8°	153	29.3

The Disruptive Influence of Reduced Pressure on Chemical Combinations.

A striking example is afforded by the work of Lemoine on hydriodic acid.[2] He shows that, with constant temperature, the less the pressure, the smaller the amount of hydrogen and iodine in combination.

Pressure. Atmospheres.	Per cent free H.	Pressure. Atmospheres.	Per cent free H.
4.5	24	0.9	26
2.3	25	0.2	29

Boussingault has proved[3] that while oxygen is absorbed by barium oxide at 450°, barium dioxide being formed, if the pressure is then removed, all the oxygen originally taken up is given off again. In other words, by means of a reduction of pressure this transformation is effected, $BaO_2 \longrightarrow BaO + O$.

Effect of a Solvent on Dissociation Tension.

Gautier has shown[4] that dry acid sodium carbonate is only very slightly dissociated in a vacuum of 10–20 mm. at 25°–30°.

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[1] Ber. d. chem. Ges., **11**, 2045.

[2] Ann. chim. phys. [5], **12**, 145.

[3] *Ibid* [5], **19**, 464.

[4] Bull. Soc. Chim., **26**, 115.

If the material is moistened the results are entirely different. When 5 grams of the material were dissolved in 20 grams of water and the solution placed in a vacuum of 300–400 mm. at 25°–30°, at the end of four days the salt was dry and consisted of about 18.7 per cent $NaHCO_3$ and 81.3 per cent Na_2CO_3. He found that water exerts the same influence on the dissociation of acid potassium carbonate, and Berthelot and André[1] obtained similar results with acid ammonium carbonate.

It is probable that a similar explanation is to be found for the differences in decomposition of dicarbonyl cuprous chloride. The material is insoluble in water, and in this instance the carbon monoxide is absorbed and given off with the greatest difficulty. It is soluble in hydrochloric acid, and similar to solutions of the acid carbonates of the alkalies, it is then decomposed much more easily. These decompositions can be readily compared by means of the curves on page 310. The break in the curve representing the decomposition of the compound made in water appears somewhat exaggerated. While there undoubtedly is a break, yet it extends only through a very short range of pressure—from about 130–160 mm.—so that a slight error in observation would lead to quite different results. I hardly think this slight irregularity sufficient reason for concluding that, when the compound is prepared in water, 1 molecule of carbon monoxide is united in a manner different from the other.

The decomposition by increased temperature of the compound made in pyridine is exactly similar to the decomposition of acetic acid and nitrogen peroxide, as can be seen from the curves.

Behavior of Inorganic Compounds containing Carbon Monoxide.

The compounds $COPtCl_2$, $(CO)_2PtCl_2$, and $(CO)_3(PtCl)_2$ (Schützenberger[2]) as well as $COPdCl_2$, $(CO)_2PdCl_2$, and $(CO)_3(PdCl_2)_2$ (Fink[3]) can be converted one into another by changing the temperature and proportion of carbon monoxide present and all are decomposed by water, the compounds $(CO)_2PtCl_2$, $(CO)_3(PtCl)_2$, $(CO)_2PdCl_2$ and $(CO)_3(PdCl_2)_2$, giving off part of their carbon monoxide as such—*e. g.*, $(CO)_2PtCl_2 + H_2O = Pt + CO_2 + 2HCl + CO$.

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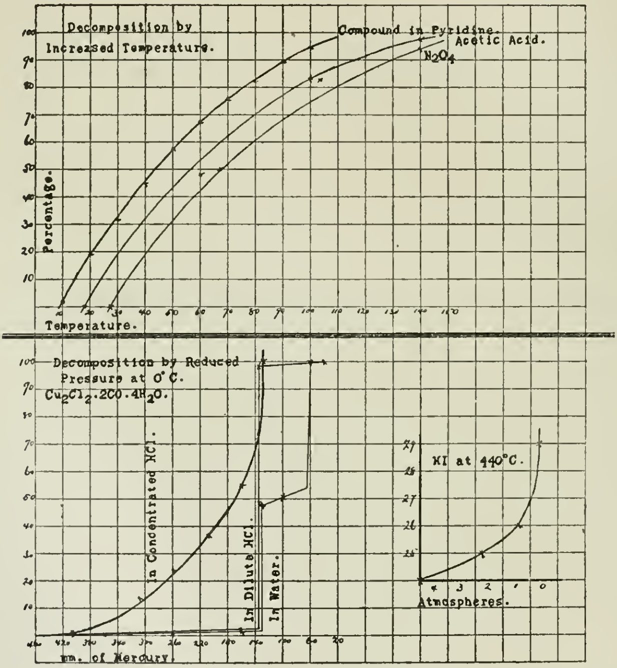
[1] Compt. rend., **103**, 665 and 716.

[2] Ann. chim. phys. [4], **15**, 100; and [4], **21**, 350.

[3] Compt. rend., **126**, 646.

When a solution of COPtCNS.KCNS (Foerster[1]) is simply evaporated, the carbon monoxide is set free, and COPtS (Foerster[2]) is decomposed by reduced pressure. All the compounds of the types $COPtCl_2$, $COPt(R)_2.2HCl$, $(CO)_2Pt(R)_2.2HCl$ (R = residue of ammonia or primary base), COPtCNS, COPtS, etc. (Foerster[3]), are decomposed by the action of potassium cyanide, carbon monoxide appearing as such.



From this very brief review I am sure we can detect great similarity between dicarbonyl cuprous chloride and these compounds, a similarity so great that one could not fail to classify it with them as a true chemical compound.

To the compound $(CO)_2CuCl_2.4H_2O$ I have given the name dicarbonyl cuprous chloride, this being in accord with the name given by Schützenberger to the analogous compound, $(CO)_2PtCl_2$.

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[1] Ber. d. chem. Ges., **24**, 2424.
[2] *Loc. cit.*
[3] *Loc. cit.*

Conclusions.

1. Carbon monoxide is not absorbed by dry cuprous chloride. It is absorbed by cuprous chloride when in hydrochloric acid solution or suspended in water.

2. As a result of this absorption a compound of definite composition is formed. This is represented by the formula $Cu_2Cl_2.2CO.4H_2O$.

3. This compound conducts itself like a true atomic compound. It is decomposed by reduction of pressure or elevation of temperature, these decompositions being similar to the decompositions of compounds, the true atomic nature of which cannot be doubted.

4. The carbon monoxide shows no marked increase in chemical activity at the moment of liberation from the compound.

5. From a comparison of dicarbonyl cuprous chloride with other inorganic compounds containing carbon monoxide, it is found to conduct itself in a manner similar to them, and deserves to be ranked as a true chemical compound.

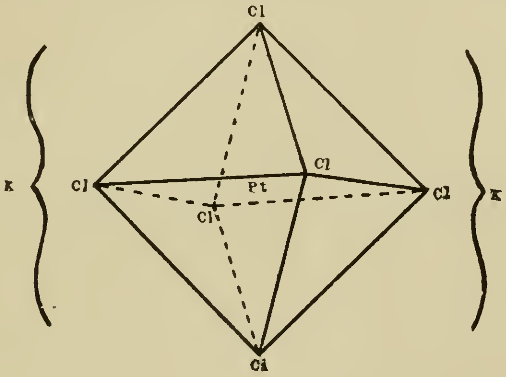
REVIEWS.

Werner's Theory of the Constitution of Inorganic Compounds.

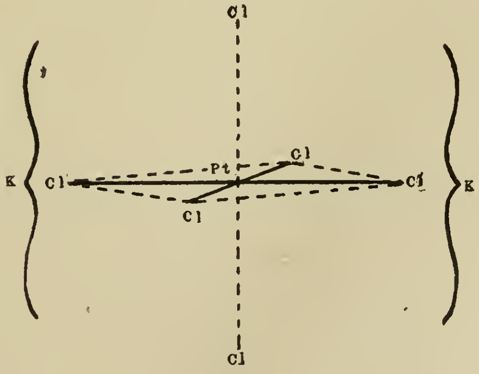
In 1893 Alfred Werner, of Zurich, published his first paper on the constitution of inorganic compounds in the Zeitschrift für anorganische Chemie. The theory there advanced, and which has since borne his name, had its origin in the inadequacy of the valence theory to account for the constitution of the metal-ammonia compounds, to which he had been devoting his attention. At this time the theories of Blomstrand as advanced in his "Chemie der Jetztzeit" and as modified and developed by Jörgensen, of Copenhagen, were generally accepted as expressing the constitution of these complex bodies. Werner's theory was promptly attacked by Jörgensen, and a vast amount of valuable work has been done by both these chemists in support of their respective views, Jörgensen's eleventh paper and Werner's twentieth paper on the subject having appeared in the Zeitschrift the present year. In addition, contributions have been made by several other chemists as K. A. Hofmann, P. Klason, and A. Cossa, while F. Reitzenstein has admirably summed up the whole subject in a recent Habilitationsschrift, and has made positive contributions to the subject in his researches on the metal-pyridin compounds. I shall not, in this paper, attempt to review in order the literature of Werner's theory, but rather to show the facts upon which the theory rests, outline the theory itself, and glance at some of the other attempts to solve the problems presented. While, undoubtedly, growing in the first place out of attempts to explain the constitution of the metal-ammonia compounds, and while the battle between Werner and Jörgensen has chiefly taken place on this field,—while, too, a large share of the arguments in support of the theory and in opposition to it have been taken from these compounds, and the theory has been worked out most completely as regards them, the application of the theory is practically to all chemical compounds.

In the metal-ammonia compounds in every well authenticated case the limit of ammonia groups is reached with six to a single positive element; as $Co(NH_3)_6X'_3$, $Cr(NH_3)_6X'_3$, etc., where X is the negative element and corresponds in number to the valence of the positive element. In the double cyanides and double nitrites, six is again the limiting number of the cyanogen or nitrite groups, as $Fe'''(CN)_6M'_3$, $Co(NO_2)_6M'_3$, and here the valence of the positive metal M′ corresponds to the valence of the iron or the cobalt in the negative group.

In one of the most common types of crystalline hydrated halides, six is the limiting number of molecules of water of crystallization, as $Ca(H_2O)_6Cl_2$, $Co(H_2O)_6Cl_2$, $Ni(H_2O)_6Br_2$. In these cases Werner considers that these groups, ammonia, cyanogen, nitrite, water are coordinated with the positive element into a group, which acts as a whole, and as a whole possesses a valence depending upon that of the positive element. Since the positive element is here coordinated with six groups, or in other cases, as $PtCl_6K_2$, with 6 atoms, it is assumed that these are arranged symmetrically around the positive element, as in the figure of an octahedron, where the positive atom occupies the center and the other elements are at the angles,



or

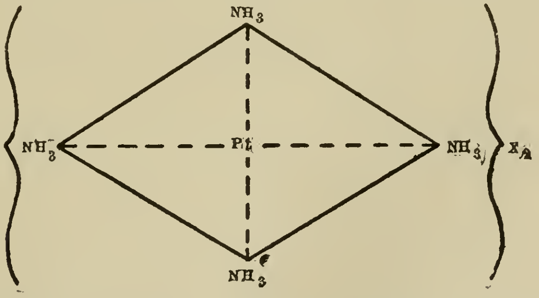


The elements united with this coordinated group are, as it were, in an outer sphere and are not in direct union with the positive element, which is thus surrounded and in some sense protected by the groups or elements of the inner sphere. The number and character of the valence of the coordinated group depends in general upon the character of the coordinated groups. Thus we have $Cr(NH_3)_6Cl_3$, the basic character of the ammonia groups rendering the whole group positive. In $[Cr(NH_3)_5Cl]Cl_2$, the group $Cr(NH_3)_5Cl$ is less basic, and has a valence of two. In $[Fe'''(CN)_6]$ the group containing the negative cyanogen is itself negative and has a valence of three; in $[Fe''(CN)_6]$ the valence is four. The determination of this valence will be considered later.

When the molecule is dissolved in water, it is dissociated electrolytically, not into positive and negative elements, but into the coordinated group on the one hand, and that with which it is united on the other hand. In the case of many of the salts this is a familiar fact, for in the old nomenclature we have for ions in solution $[Cr(\overset{+}{N}H_3)_6],3[\overset{-}{Cl}]$; $[Cr(\overset{+}{N}H_3)_5Cl],2[\overset{-}{Cl}]$; $3[\overset{+}{K}],[Fe'''(\overset{-}{C}N)_6]$; $4[\overset{+}{K}],[Fe(\overset{-}{C}N)_6]$; $2[\overset{+}{K}],[\overset{-}{Pt}Cl_6]$; this being shown both by electrical conductivity determinations and also by the precipitation of these negative ions, whether simple or complex, by silver nitrate. The application of this idea to the case of hydrated salts appears less familiar. In our ordinary halide salts we assume that the halide is directly united to the metal, thus Na—Cl, and that in solution this is dissociated into sodium ions and chlorine ions. Yet it has been universally agreed that in the ammonia bases the ionized halide atom or other negative group is not directly united to the metal. According to the generally accepted Blomstrand-Jörgensen theory, a halogen directly connected with the metal is not ionizable, but only such as are connected with it through the medium of ammonia. Thus, in the salts of the purpureo series as $[Cr(NH_3)_5Cl]Cl_2$ the two chlorine atoms which are connected with chromium indirectly are alone precipitated by silver nitrate in the cold, while the other chlorine atom which is directly connected with the chromium is not thus precipitable, nor is it dissociated in solution. Now the old theory makes no pretense of resolving the inconsistency that, in the one case, a chlorine atom directly united to a metal is not ionizable, while in the other case it is. According to Werner, when, for example, $Co(H_2O)_6Cl_2$ is dissolved in water, the ions are not $[\overset{+}{Co}]$ and $2[\overset{-}{Cl}]$, but are $[Co(\overset{+}{H}_2O)_6],2[\overset{-}{Cl}]$. Here as in the ammonia bases, the halogen is not directly connected with the metal, but with the group $[Co(H_2O)_6]$, in which the cobalt atom is surrounded by the water molecules in the inner sphere, and, so to speak, protected by them from direct contact with the halogens.

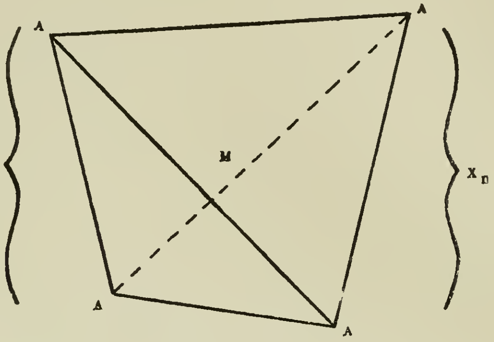
In order then that a salt may become dissociated in solution, it is necessary that the metal shall be surrounded by a number of other units which may be ammonia or cyanogen, or nitrite groups or single atoms (as the single chlorine atom in the purpureo salts), but which are most frequently water molecules. It is interesting to note that in this point Werner's theory, while availing itself of the theory of electrolytic dissociation in aqueous solution, approaches very closely to the general principles of the hydrate theory of solutions; indeed it really harmonizes the two apparently irreconcilable and mutually exclusive theories, both of which rest upon a substratum of undeniable facts.

Not all compounds can be explained, however, according to the type $M(A)_6$. In the platinum-ammonia bases, for instance, the limiting number of the ammonia groups appears to be four for each platinum atom, and among the metal-ammonia compounds in general we find very common the type $M(NH_3)_4.X_2$. Here there are four groups or atoms directly coordinated with the positive element. This is explained by assuming a configuration of the molecule in a plane; that is, one axis, in the figure of the first type, is wanting. Thus:

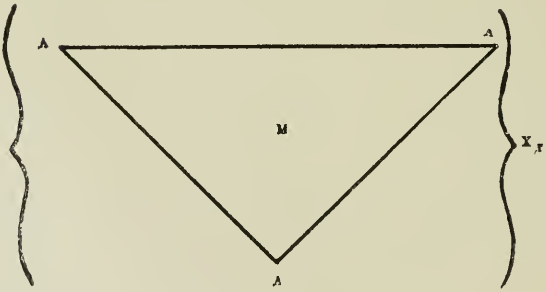


Of this type we have in other classes of compounds $[Pt(CN)_4]K_2$, $[CuCl_4]K_2$, $[Cu(NO_3)_4](NH_4)_2$, $[HgBr_4]K_2$, $[Cd(NH_3)_4]Br_2$, $[Cd(H_2O)_4]Cl_2$, $[Mn(H_2O)_4]SO_4$, and many others. Compounds of this type may pass into those of the first type by two further groups or atoms becoming coordinated with the positive element, as in the formation of the platinibases from the platino-bases, $[Pt(NH_3)_4]Cl_2$, $[Pt(NH_3)_4Cl_2]Cl_2$; $[Cu(NH_3)_4]Cl_2$, $[Cu(NH_3)_6]Cl_2$, and $[Cu(NH_3)_4(H_2O)_2]Cl_2$.

These two types have been most completely worked out by Werner, but there seems to be evidence of the existence of perhaps several other types. Thus, while some compounds of the second type, $[MA_4]X_n$, may be represented by the plane configuration, in other cases the coordinated group may be represented by the tetrahedron. To this latter, which would be of the same general formula $[MA_4]X_n$, there would correspond a plane configuration of the type $[MA_3]X_n$, or graphically



and



This need not indeed exhaust the possibilities, but thus far no compound seems to have been noticed in which one atom has a higher coordination number than six.

There seem to be several factors which have an influence in determining the coordination number of an element. The nature of the individual atom, that of the coordinated groups or atoms, and that of the atoms or groups of the outer sphere, are all of influence, though insufficient work has as yet been done to determine the relative importance of each factor. That the molecular weight of the coordinated groups is of influence is shown by Reitzenstein's comparison of the hydrates, ammonia compounds and pyridine compounds. While in many cases there is great resemblance between the two former, and at least one series is known, $CuSO_4,5H_2O$; $CuSO_4,NH_3,4H_2O$; $CuSO_4,2NH_3,3H_2O$; $CuSO_4,3NH_3,2H_2O$; $CuSO_4,4NH_3,H_2O$; and $CuSO_4,5NH_3$, in which each transition stage from the hydrate to the ammonia compound is known, in the case of pyridine the coordination number in only two cases reaches a maximum of six, these being $[CdPyr_6]Br_2$ and $[CdPyr_6]I_2$. Here too the influence of the halogen is apparent, for all efforts have failed to obtain a cadmium chloride containing more than 2 molecules of pyridine. A salt $[CoPyr_3(H_2O)_3]Cl_2$ is, however, known, and in several of the ammonia-pyridine-platini bases, the coordination number of the platinum atom is six, though in no case are more than four pyridine atoms present.

Two influences must necessarily affect the coordination number: one, the size of the coordinated group or atom, or perhaps we should better say the space it occupies, a point to which no inconsiderable attention has been given of late years as regards the carbon atom; and the other the character and intensity of its motion. Perhaps also the relative kind and phase of the motion of the central atom and of those coordinated with it may play a part, as suggested by Venable in his recent paper on the nature of valence.

Having thus sketched Werner's theory in broad outlines, we must next examine its application to certain classes of compounds, to gain a more complete knowledge of it and to see how far it is consistent with facts.

Type $[MA_6]X_n$.—Taking up first this type, especially in its application to the metal-ammonia compounds of the type $[MA_6]X'_3$, we find an almost complete series of compounds, each with successively one ammonia group less than the preceding. The luteo salts $[M(NH_3)_6]X_3$, for example, $[Co(NH_3)_6]Cl_3$, by loss of one ammonia group pass into the purpureo salts $[M(NH_3)_5]X_3$. But in the purpureo salts only two of the chlorine atoms are ionized in solution. We should therefore represent these salts as $\left[M\begin{matrix}(NH_3)_5\\X\end{matrix}\right]X_2$. The xantho salts as $\left[Co\begin{matrix}(NH_3)_5\\NO_2\end{matrix}\right]X_2$ are of this class.

Next come the croceo salts, $M(NH_2)_4X_3$, and here but one halogen is ionized, hence the formula $\left[M\begin{matrix}(NH_3)_4\\(NO_2)_2\end{matrix}\right]X$.

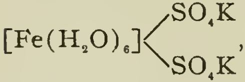
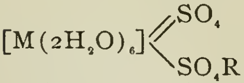
In $\left[Co\begin{matrix}(NH_3)_3\\(NO_2)_3\end{matrix}\right]$ we have, according to Werner, a compound which is not a conductor of electricity and hence is not electrolytically dissociable. In the next group we find $\left[Co\begin{matrix}(NH_3)_2\\(NO_2)_4\end{matrix}\right]K$, and $\left[Co\begin{matrix}(NH_3)_2\\(SCN)_4\end{matrix}\right]NH_4$; and in the last member of the series many salts of the general type $[MX_6]R'_3$, such as $[Co(NO_2)_6]K_3$; $[Fe(CN)_6]K_3$; $[CrF_6]K_3$; $[Fe(SCN)_6]K_3$; and $[RhCl_6]K_3$. In this series we notice that as each ammonia group is removed, an atom of the outer sphere replaces it in the coordinated group, and hence the valence of the coordinated group is lessened by one. With the removal of three ammonia groups the basicity of the coordinated group disappears, and its valence becomes zero. With the further removal of ammonia it becomes positive, and the positive valency increases step by step. Thus the valence of the coordinated group is equal to the valence of the central atom minus the number of negative atoms or groups coordinated with it, a negative number representing valence toward positive elements.

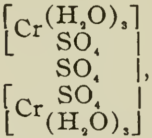
A second class of compounds of the type $[M(NH_3)_6]X_n$ is that derived from quadrivalent metals. This class includes the great number of the platini-ammonia bases, as well as ammonia compounds of quadrivalent tin, titanium, and silicon. Examples of the member with the largest number of ammonia groups are $[Pt(NH_3)_6]Cl_4$, $[Sn(NH_3)_6]I_4$, $[Ti(NH_3)_6]Cl_4$, $[Si(NH_3)_6]Cl_4$. From this formula may be derived, by loss of ammonia, compounds similar to those of the first class. Few of these are as yet known. Joly's tetrammonium-nitroso-ruthenium base, as $\left[Ru\begin{matrix}NO\\OH\\(NH_3)_4\end{matrix}\right]Cl_2$ and $\left[Ru\begin{matrix}NO\\Cl\\(NH_3)_4\end{matrix}\right]Cl_2$ probably belongs to the division, in which two of the ammonia groups are lost, being replaced by un-ionizable groups or elements. The next division is represented by the platimonodiammine bases $\left[Pt<\begin{matrix}Cl_3\\(NH_3)_3\end{matrix}\right]Cl$, where there is but one ionizable chlorine atom. The plati-ammine salts, as $\left[Pt\begin{matrix}(NH_3)_2\\Cl_4\end{matrix}\right]$ can be heated with concentrated sulphuric acid without losing chlorine, and hence represent the case where, by the loss of four ammonia groups, all four chlorine atoms have become coordinated with the platinum atom.

In the next division is the salt $\left[Pt\begin{matrix}NH_3\\Cl_5\end{matrix}\right]K$, when by the loss of a further ammonia group the whole coordinated group has become negative and univalent. The salt $\left[Pt\begin{matrix}Pyr\\Cl_5\end{matrix}\right]Pyr$ may also be placed here, though the formula suggested for it by Jörgensen is much more complex. The limiting member of this class is $[MX_6]R_2$, to which belong the familiar salts $[PtCl_6]K_2$, $[SiF_6]K_2$, $[TiF_6]K_2$, $[SnF_6]K_2$, and $\left[Ru\begin{matrix}NO\\Cl_5\end{matrix}\right]K_2$, as well as many others. Incidentally I may add that in accordance with the analogy $AuCl.KCl$, $PtCl_2.2KCl$, $RhCl_3.3KCl$, we should be led to expect $PtCl_4.4KCl$ and $RuNOCl_3.3KCl$, or $RuNOCl_3.4KCl$, yet, as a matter of fact, the number of halogen atoms in the double halides of quadrivalent metals is always limited to six, a fact difficult to account for on the valence theory, and in which it seems necessary to consider the space relations of the atoms.

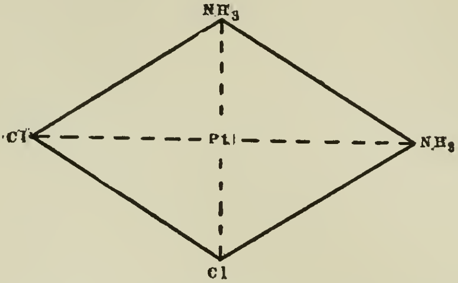
The third class of compounds, of the type $[M(NH_3)_6]X_n$ is that in which M is a bivalent metal and the number of negative atoms is consequently also two. The number of compounds known in this field is much smaller than in the former cases, though it may well be that when the complex compounds are studied from the standpoint of the Werner theory, many of the theoretically possible compounds will be discovered. Of the first division of this class a very considerable number of compounds are known, as $[Ni(NH_3)_6]Cl_2$, $[Cu(NH_3)_6]Br_2$, $[Cd(NH_3)_6](NO_3)_2$, $[Co(NH_3)_6]SO_4$, and many others. To the last division of the class, where all the ammonia has been removed and hence replaced by negative groups, the coordinated group therefore becoming negative and quadrivalent, we have the familiar class of double cyanides, as $[Fe(CN)_6]K_4$, $Cr[(CN)_6]K_4$, $[Ru(CN)_6]K_4$, as well as such salts as $[Ni(NO_2)_6]K_4$ and $[CdCl_6]K_4$. Of the intermediate divisions, Werner has found but a single representative, $\left[Cu\begin{smallmatrix}(NH_3)_2\\Cl_4\end{smallmatrix}\right](NH_4)_2$.

There is another class of compounds of this first general type in which the ammonia groups have been, to a greater or less extent, replaced by water, the compounds to which Palmaer has given the name aquo-ammonia bases. When one of the ammonia groups is substituted by water we have the roseo compounds which are known in the cobalt, chromium, rhodium, and iridium series, of which $\left[Co\begin{smallmatrix}(NH_3)_5\\H_2O\end{smallmatrix}\right]Cl_3$ is an example. In these compounds the water is very different from water of crystallization, and cannot be removed without changing completely the character of the salt. In the roseotetrammine salts of Jörgensen, we have two ammonia groups replaced by water, without affecting the valence of the coordinated group, as $\left[Co\begin{smallmatrix}(NH_3)_4\\(H_2O)_2\end{smallmatrix}\right]Cl_3$. Salts where 3 molecules of water are replaced by water are known, and the limiting member where all the six ammonia groups are replaced by water belongs to a very common type, as $[Al(H_2O)_6]Cl_3$, $[Cr(H_2O)_6]Cl_3$, $[Fe(H_2O)_6]Cl_3$. Of the other classes of this type, numerous compounds are known in which the ammonia is more or less replaced by water, and the final member, where all the ammonia is thus replaced, brings us to the commonest type of hydrate, as $[Ni(H_2O)_6]Cl$, $[Mg(H_2O)_6]Cl_2$, $[Sr(H_2O)_6]Br_2$, $[Sr(H_2O)]_6(IO_4)_2$, $[Sr(H_2O)_6]S_4O_6$, $[Zn(H_2O)_6]S_2O_6$, etc. From this Werner draws the conclusion that the property of metallic salts to unite with 6 molecules of water and with 6 molecules of ammonia, has the same cause, and that this cause rests in the nature of the metallic atom.

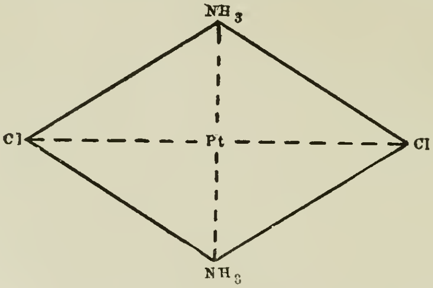
Certain familiar salts do, however, unite with more than 6 molecules of water, especially many of the vitriols. Thus we have, for example, $FeSO_4.7H_2O$. Here, however, the acid radical plays a part, as it is well known that several hydrates of sulphuric acid exist. One of these water molecules can be considered as being united structurally with the SO_4 group, indeed, as a matter of fact, the compound holds one of these water molecules with much more firmness than the other six. This we should write $[Fe(H_2O)_6]SO_4.H_2O$ or $[FeSO_4(H_2O)_6]SO_5H_2$. The number of 6 molecules of water recurs again in the double sulphates, where we have  $[Fe(H_2O)_6]\begin{matrix} SO_4K \\ SO_4K \end{matrix}$, etc. The alums form an exception to this rule, but may be explained by assuming that in some cases the double water molecule acts as a unit, as it is believed to do in water itself. Thus an alum will have the formula  $[M(2H_2O)_6]\begin{matrix} SO_4 \\ SO_4R \end{matrix}$, the number six again appearing.

Finally, to this first general type belong also a large number of salts in which more or less water is present in the coordinated group. Space permits only mere mention of examples. Of the type $\left[M \begin{smallmatrix} (H_2O)_5 \\ X \end{smallmatrix}\right] X_2$ we have one form of chromium chloride, in which only two-thirds of the chlorine can be precipitated by silver nitrate. Of the type $\left[M \begin{smallmatrix} (H_2O)_3 \\ X_3 \end{smallmatrix}\right]$ we have a chromium sulphate,  $\begin{bmatrix} \left[Cr \begin{smallmatrix} (H_2O)_3 \\ SO_4 \end{smallmatrix}\right] \\ SO_4 \\ \left[Cr \begin{smallmatrix} SO_4 \\ (H_2O)_3 \end{smallmatrix}\right] \end{bmatrix}$, of which Recoura has shown that in the freshly prepared solution no precipitate is formed by barium chloride. The type $\left[M \begin{smallmatrix} (H_2O)_2 \\ X_4 \end{smallmatrix}\right] R$ has as example $\left[Au \begin{smallmatrix} Cl_4 \\ (H_2O)_2 \end{smallmatrix}\right] K$, etc. The double salts of the formula $\left[M\begin{smallmatrix}H_2O\\X_5\end{smallmatrix}\right]K_3$ are very common, as $\left[Cr\begin{smallmatrix}F_5\\H_2O\end{smallmatrix}\right]K_2$, $\left[Al\begin{smallmatrix}Cl_5\\H_2O\end{smallmatrix}\right]K_2$, $\left[Rh\begin{smallmatrix}Cl_5\\H_2O\end{smallmatrix}\right](NH_4)_2$, $\left[Mn\begin{smallmatrix}F_5\\H_2O\end{smallmatrix}\right][Co(H_2O)_6]$. Among the double salts of bivalent metals we find the following: Of the type $\left[M\begin{smallmatrix}(H_2O)_3\\X_3\end{smallmatrix}\right]R$ we have $\left[Mn\begin{smallmatrix}Cl_3\\(H_2O)_3\end{smallmatrix}\right]Li$, $\left[Cu\begin{smallmatrix}Cl_3\\(H_2O)_3\end{smallmatrix}\right]K$, etc.; of the type $\left[M\begin{smallmatrix}(H_2O)_2\\X_4\end{smallmatrix}\right]R_2$ we have $\left[Fe\begin{smallmatrix}Cl_4\\(H_2O)_2\end{smallmatrix}\right]K_2$, $\left[Co\begin{smallmatrix}F_4\\(H_2O)_2\end{smallmatrix}\right](NH_4)_2$, etc. The substance of the matter regarding the compounds of this first general type is summed up by Werner in these words. In the metal-ammonia salts, as well as in the hydrates (as far as concerns the normal compounds) and also in the double salts thus far considered, we must assume the group MA_6, in which all the ammonia molecules, water molecules, or acid radicals are directly connected with the metal atom, since it is in no other way possible to account for their reciprocal relations.

Type $[MA_4]X_n$.—A second type of compounds must now be considered in which the number four appears to play the same rôle as the number six in the first type. These are the compounds in which the metal is coordinated with four groups, and may be derived from the octahedral conformation by the loss of one axis, and hence the group will have a plane configuration, or it may in other cases be considered as represented by the tetrahedron. It is probable that both forms exist in different compounds, and the group may perhaps pass from one form to the other. It is unnecessary to dwell upon this type at length, as its theory will be easily understood from the extended description of the compounds of the first type. The ammonia compounds of this type are numerous, and include the plato-diammine salts $[Pt(NH_3)_4]X_2$, as well as the corresponding diammine salts of palladium. Here also belong many other metal-ammonia salts as $[Cu(NH_3)_4]Cl_2$, $[Ni(NH_3)_4](SCN)_2$, etc. With the loss of one ammonia we have the platomonodiammine salts $\left[Pt\begin{smallmatrix}(NH_3)_3\\Cl\end{smallmatrix}\right]Cl$, which form with chloroplatinous acid the salt $\left[Pt\begin{smallmatrix}(NH_3)_3\\Cl\end{smallmatrix}\right]_2Pt''Cl_4$, and not $Pt(NH_2)_3.PtCl_4$, which would be the case if both atoms of chlorine were ionizable. To the division $\left[M\begin{smallmatrix}(NH_3)_2\\X_2\end{smallmatrix}\right]$ belong the platosammine and the platosemidiammine compounds $\left[Pt\begin{smallmatrix}(NH_3)_2\\Cl_2\end{smallmatrix}\right]$. Neither of these compounds unites with chloroplatinous acid, and hence both must be ranked as neutral compounds, as would be expected from Werner's theory. Their isomerism is explained by Werner as stereoisomerism, the platosammine chloride being the *cis* form



and the platosemidiammine chloride being the *trans* form

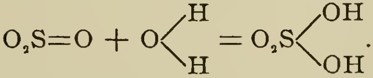


Two salts recently discovered by Cossa complete the series. These are $\left[\mathrm{Pt}^{\mathrm{NH_3}}_{\mathrm{Cl_3}}\right]\mathrm{K}$ and $\left[\mathrm{Pt}^{\mathrm{Pyr}}_{\mathrm{Cl_3}}\right]\mathrm{K}$. Here the loss of the third ammonia group and entrance into the coordinated group of the third negative atom, render the group itself negative and univalent. Finally we have the last division, where all the ammonia is replaced by negative atoms or groups, in the familiar type $[\mathrm{MX_4}]\mathrm{R_2}$, of which $[\mathrm{PtCl_4}]\mathrm{K_2}$, $[\mathrm{Cu(NO_3)_4}](\mathrm{NH_4})_2$, $[\mathrm{Pd(CN)_4}]\mathrm{K_2}$, $\left[\mathrm{Hg}^{\mathrm{I_2}}_{\mathrm{Br_2}}\right]\mathrm{K_2}$, $[\mathrm{Pt(NO_2)_4}]\mathrm{K_2}$, are a few of the many examples which might be cited.

In this type also the ammonia can be replaced, as in the first, by water. This is perhaps as well illustrated by the copper sulphate series as any, when we have $[\mathrm{Cu(NH_3)_4}]\mathrm{SO_4.H_2O}$, $\left[\mathrm{Cu}^{\mathrm{(NH_3)_3}}_{\mathrm{H_2O}}\right]\mathrm{SO_4.H_2O}$, $\left[\mathrm{Cu}^{\mathrm{(NH_3)_2}}_{\mathrm{(H_2O)_2}}\right]\mathrm{SO_4.H_2O}$, $\left[\mathrm{Cu}^{\mathrm{(NH_3)}}_{\mathrm{(H_2O)_3}}\right]\mathrm{SO_4.H_2O}$, and $[\mathrm{Cu(H_2O)_4}]\mathrm{SO_4.H_2O}$, though many other examples are known. Finally, we have as hydrated salts of this type $\left[\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{F_3}}{\mathrm{H_2O}}\right]\mathrm{K}$, $\left[\mathrm{Sn}\genfrac{}{}{0pt}{}{\mathrm{Br_3}}{\mathrm{H_2O}}\right]\mathrm{K}$, $\left[\mathrm{Hg}\genfrac{}{}{0pt}{}{\mathrm{Cl_3}}{\mathrm{H_2O}}\right]\mathrm{K}$, etc., members of the other divisions not being known.

That other types than the two thus far discussed may exist is by no means improbable, indeed there is reason to believe that certain elements as columbium and uranium may in certain cases have a coordination number of eight, but such cases have not been worked out thus far.

It seems quite possible that certain elements as nitrogen and boron have the coordination configuration of the tetrahedron with the coordination number of four. Here boron being more positive than carbon, when coordinated with negative atoms, furnishes a negative group as $[BF_4]K$; while nitrogen being more negative than carbon, forms a positive coordination group, as $[NH_4]Cl$ and $[N(C_xH_y)_4Cl$. In both cases the valence of the group is the difference between the valence of the element and that of the elements or groups with which it is coordinated.

Thus far the application of the theory of Werner to one large class of compounds, the oxygen salts, has not been touched upon, and this must now be considered briefly. According to the ordinary theories there are two classes of oxides, the acid-forming and the base-forming oxides. A salt is formed by the union of one oxide of each class, but as the terms acid-forming and base-forming are only relative, a salt may be defined as the compound formed by the union of two oxides. Similarly an acid, which is a hydrogen salt, is formed by the union of an acid-forming oxide with water. According to the valence theory, in the formation of an oxyacid there is assumed the tendency of the doubly-bound oxygen atom of the oxide to unite with the separated hydrogen and hydroxyl of water to form two hydroxyl groups, thus . At first sight, such union of two oxides to form a salt would seem to have little in common with the union of two chlorides to form a double chloride, but in reality the two reactions are analogous. That salt and acid formation is not dependent upon hydroxyl formation, is rendered probable by two facts. First, considering the union with water to form acids, not all oxides of so-called negative nature will unite with water. The oxides RuO_4 and OsO_4, for example, in spite of their extreme amount of oxygen, are not acid-forming but neutral substances, and will not unite with water. Second, the union of oxides with water is always (save perhaps exceptionally in the per-iodic acids) limited to the formation of compounds with four atoms of oxygen.

Thus, according to the valence theory, there is no reason why SO_3 should not form H_4SO_5 and P_2O_5 should not form H_5PO_5. Further, we find that the halogen compounds unite with water as well as the oxides, though the valence theory is responsible, for our habit of considering as of entirely different character these compounds which are really analogous.

Thus far, in considering the coordinated atoms and groups, these have been confined to either non-valent or saturated groups such as water and ammonia, and to univalent elements or groups such as chlorine. The first question which arises is whether a bivalent atom like oxygen entering a coordinated group will replace one or two of the groups or atoms we have been considering. This question would seem to be settled by the considerable class of oxyfluorides, where we have such a substitution; thus $[VF_6]K_3$, $\left[V\begin{matrix}O\\F_5\end{matrix}\right]K_2$,

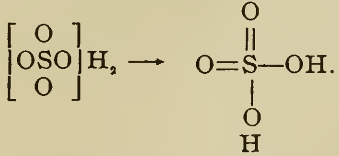
$$\left[\begin{matrix}O_2\\VF_3\\H_2O\end{matrix}\right][Zn(H_2O_6)],\qquad \left[Mo\begin{matrix}O\\F_5\end{matrix}\right](NH_4)_2,\qquad \left[\begin{matrix}O_2\\MoF_3\\H_2O\end{matrix}\right]K_2,$$

$\left[Mo\begin{matrix}O_3\\F_3\end{matrix}\right](NH_4)_3$, as well as similar compounds of tungsten and columbium. We have also the compounds $\left[Mo\begin{matrix}O_2\\(CN)_4\end{matrix}\right]K_2$ and $\left[Mo\begin{matrix}S_2\\(CN)_4\end{matrix}\right]K_2$, all of which show that, when oxygen or sulphur enters the coordinated group, it occupies one place only, that is one coordination position. We come thus to the conclusion that the formation of oxy-salts is to be attributed to the same cause as the formation of the so-called coordination compounds which we have already considered. Thus, comparing them, we have $\begin{matrix}O\\OS\\O\end{matrix} + OH_2 = \left[\begin{matrix}O\\OSO\\O\end{matrix}\right]H_2$, similar to $\begin{matrix}Cl\\ClAu\\Cl\end{matrix} + ClH = \left[\begin{matrix}Cl\\ClAuCl\\Cl\end{matrix}\right]H$. Indeed, we can cite the formation of compounds of intermediate type, thus justifying our placing the two above reactions in the same class. For example, $\begin{matrix}O\\OCr\\O\end{matrix} + ClK = \left[\begin{matrix}O\\OCrCl\\O\end{matrix}\right]K$ and $\begin{matrix}F\\FAl\\F\end{matrix} + O(C_2H_5)_2 = \left[\begin{matrix}F\\FAlO\\F\end{matrix}\right](C_2H_5)_2$.

What has here been said will apply equally well to all oxysalts. In by far the largest number of cases the type of the coordination group is MO_4. Thus we have $[SiO_4]H_4$,

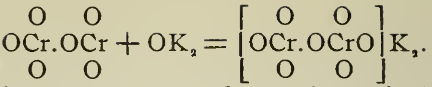
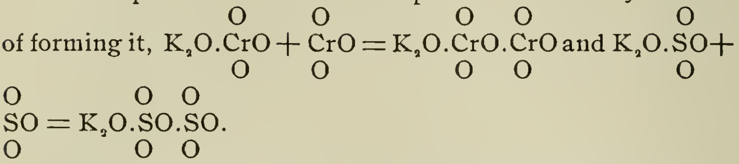
$[PO_4]H_3$, $[SO_4]H_2$, $[ClO_4]H$, and $[RuO_4]$, and in passing thus from the fourth to the eighth group of the periodic table, it becomes apparent why RuO_4 forms no salts. It is also seen that the oxygen number remains the same while the number of hydrogen atoms decreases, although according to the valence theory the valence of the elements regularly increases until the valence of ruthenium reaches eight. The coordination type of $[MO_6]$ appears to occur in only a single instance, that of the per-iodates, $[IO_6]H_5$ and $[IO_6]_2Ba_5$.

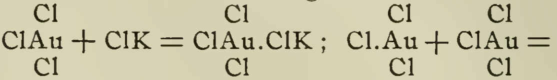
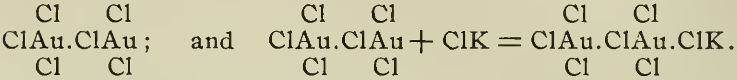
The oxy-salts are thus to be considered as molecular compounds, even as the double halides, and in this same category we have the sulphur, selenium, and probably the tellurium salts. It is perhaps the greatest advantage of Werner's theory that it furnishes a general principle to include all of these compounds, which, though chemically analogous, are by the valence theory explained in very different ways. It is not at all impossible that in some cases these molecular compounds, conditioned by the bivalence of oxygen and the rapid motion of the hydrogen atom, can go over into true valence compounds, as, for example, in sulphuric acid,



$$\left[\begin{array}{c} O \\ OSO \\ O \end{array}\right]H_2 \longrightarrow \begin{array}{rcl} & O & \\ & \| & \\ O{=} & S & {-}OH. \\ & | & \\ & O & \\ & H & \end{array}$$

If we now consider the spacial configuration of the coordinated group $[MO_4]$, the tetrahedron seems probable, and we might expect to find the corresponding plane configuration. There are indeed quite a considerable number of compounds which belong to this type. Among these are carbonic acid, $\left[\begin{array}{ccc} & O & \\ & C & \\ O & & O \end{array}\right]H_2$; formic acid, $\left[\begin{array}{ccc} & O & \\ & C & \\ O & & H \end{array}\right]H$; formic aldehyde, $\left[\begin{array}{ccc} & O & \\ & C & \\ H & & H \end{array}\right]$; metasilicic acid, $\left[\begin{array}{ccc} & O & \\ & Si & \\ O & & O \end{array}\right]H_2$; nitric acid, $\left[\begin{array}{ccc} & O & \\ & N & \\ O & & O \end{array}\right]H$; metaphosphoric acid, $\left[\begin{array}{ccc} & O & \\ & P & \\ O & & O \end{array}\right]H$.

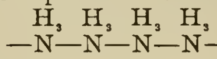
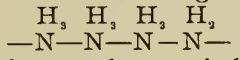
The case of the derivatives of the polymerized oxides would be explained by two or more oxides becoming coordinated, thus $O\overset{O}{\underset{O}{Cr}} + O\overset{O}{\underset{O}{Cr}} = O\overset{O}{\underset{O}{Cr}}.O\overset{O}{\underset{O}{Cr}}$ and in the cases where the polymerized oxides are stable, we should have the formation of the salt as follows:  $\overset{O}{\underset{O}{OCr}}.\overset{O}{\underset{O}{OCr}} + OK_2 = \left[\overset{O}{\underset{O}{OCr}}.\overset{O}{\underset{O}{OCrO}}\right]K_2$. This conception of the salt corresponds to the ready method of forming it,  $K_2O.\overset{O}{\underset{O}{CrO}} + \overset{O}{\underset{O}{CrO}} = K_2O.\overset{O}{\underset{O}{CrO}}.\overset{O}{\underset{O}{CrO}}$ and $K_2O.\overset{O}{\underset{O}{SO}} + \overset{O}{\underset{O}{SO}} = K_2O.\overset{O}{\underset{O}{SO}}.\overset{O}{\underset{O}{SO}}$.

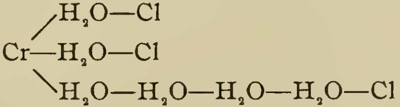
The case is the same in the halogen salts where we have similarly  $\overset{Cl}{\underset{Cl}{ClAu}} + ClK = \overset{Cl}{\underset{Cl}{ClAu}}.ClK$; $\overset{Cl}{\underset{Cl}{Cl.Au}} + \overset{Cl}{\underset{Cl}{ClAu}} =$  $\overset{Cl}{\underset{Cl}{ClAu}}.\overset{Cl}{\underset{Cl}{ClAu}}$; and $\overset{Cl}{\underset{Cl}{ClAu}}.\overset{Cl}{\underset{Cl}{ClAu}} + ClK = \overset{Cl}{\underset{Cl}{ClAu}}.\overset{Cl}{\underset{Cl}{ClAu}}.ClK$. That these polymerized halides are sometimes very stable is shown by the vapor-density of aluminum chloride.

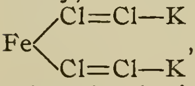
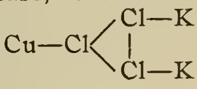
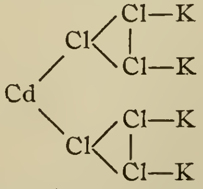
It is to be noted further that while with some elements the limiting coordination number is six and with others four, this end type of spacial or plane configuration is not always reached. Owing to less energy of the uniting molecules or other causes, the limit may be sooner reached, as for example, $Ag(CN)_2K$, $Cu(CN)_2K$.

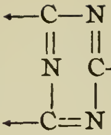
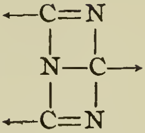
It is according to the same idea that the complex acids of molybdenum, tungsten, etc., are to be explained, where a large number of the oxide groups are polymerized together in stable form. Just what may be the structure of such highly polymerized groups it is now not possible to say, beyond that in all probability it is spacial.

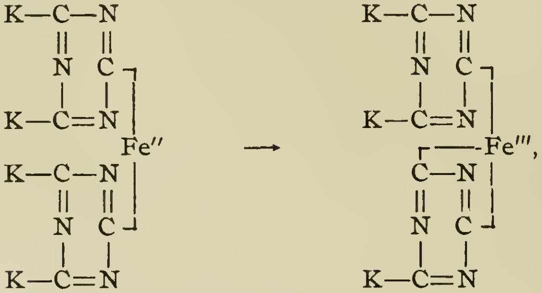
We have thus sketched the features of Werner's theory, which is necessarily incomplete. It has required more than half a century to bring the valence theory to its present form, and yet, when it reaches the structure of molecular compounds, in by far the greater number of such compounds, it utterly breaks down.

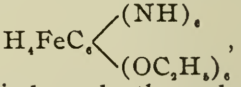
It remains to point out some of the weaknesses of the application of the valence theory to some of these molecular compounds. In its application to the metal-ammonia salts the theory in the hands of Jörgensen, who in this field is master, has two weak points. First, while it applies well to the more stable of these bases, as those of cobalt, chromium, platinum, etc., the same principles are not applicable to the less stable of these ammonia compounds as those of copper, zinc, nickel, etc., yet the chemical difference between these compounds is not one of kind but of degree. Nor does it take any possible cognizance of the fact that in many of these less stable ammonia compounds, the ammonia can be replaced in part or in whole by water. It is a theory which applies to only one particular class of ammonia compounds. Second, it assumes the existence of the group  $-\overset{H_3}{N}-\overset{H_3}{N}-\overset{H_3}{N}-\overset{H_3}{N}-$ and even the group  $-\overset{H_3}{N}-\overset{H_3}{N}-\overset{H_3}{N}-\overset{H_2}{N}-$ in stable compounds.

Now from what we know of the nitrogen atom, such a group would necessarily be exceedingly unstable. Even compounds of two nitrogen atoms united N—N are far from stable, and it is hardly conceivable that the N_4 group should be of such remarkable stability. Since, however, there is no limit to the substitution of ammonia groups by water we are led to a formula of  $Cr\left<\begin{matrix}H_2O-Cl\\H_2O-Cl\\H_2O-H_2O-H_2O-H_2O-Cl\end{matrix}\right.$ for the hydrated aluminum chloride, which would hardly be agreed to by the most pronounced adherent of the valence theory.

To explain the double chlorides according to the valence theory Remsen has used a development of the Blomstrand theory, assuming the bivalent groups Cl_2, F_2, thus:  $Fe\left<\begin{matrix}Cl=Cl-K\\Cl=Cl-K\end{matrix}\right.$, etc. So long as the number of the alkaline salt molecules is no greater than that of the halogen atoms in the halide, this explanation might serve, but when this number becomes greater, as is sometimes the case, it becomes necessary to assume the trivalent Cl_3 group, as  $Cu-Cl\left<\begin{matrix}Cl-K\\|\\Cl-K\end{matrix}\right.$ for CuCl.2KCl and  $Cd\left<\begin{matrix}Cl\left<\begin{matrix}Cl-K\\|\\Cl-K\end{matrix}\right.\\Cl\left<\begin{matrix}Cl-K\\|\\Cl-K\end{matrix}\right.\end{matrix}\right.$ for $CdCl_2.4KCl$. But this explanation covers only the double halides. The double cyanides and double nitrites which it is reasonable to consider are analogous, must be otherwise accounted for.

The efforts to elucidate the structure of the double cyanides have been many but unsatisfactory. Graham assumed in the double iron cyanides the special trivalent group $(CN)_3$; Blomstrand used his chain formulæ; Erlenmeyer using Graham's $(CN)_3$, gives it the structure , while others have suggested . Aside from the improbability of representing the change of $K_4Fe(CN)_6$ into $K_3Fe(CN)_6$ by the formulae



thus writing the two $(CN)_6$ groups differently with the iron and potassium, there stand, first, Freund's conversion of hydrogen ferrocyanide into the imido ether,  $H_4FeC_6{<}^{(NH)_6}_{(OC_2H_5)_6}$, where each cyanogen group has acted independently, and, second, the existence of the nitroprussides so-called, where one of the six cyanogens is replaced by the nitroso group.

Even if these explanations were all satisfactory in themselves, there would still be the objection that many obviously related and often closely related compounds are explained on various different principles.

I have not attempted to touch on the development of Werner's theory in its interesting application of stereoisomerism to inorganic compounds save in a single instance, from the fact that there is still too much doubt about those cases which are possibly to be included in this field. Nor have I touched upon the objections to the theory especially as urged by Jörgensen. These objections seem to me to attack its application to special compounds, and especially to those compounds whose doubtful isomerism, as well as constitution, are not essential to the theory. I do not think that valid objections to the theory in its larger lines have yet been brought forward.

It is true that the conception of the coordinated group is one new and strange to our present chemical ideas, but the same was true of the electrolytic dissociation of salts in solution, and the idea of a free ion is still difficult for some of us to grasp. Of the nature of valence itself we know little or nothing, and it is by no means impossible that, if the nature of valence were known to us, the nature of coordination would also become clear.

Werner's theory is doubtless not the whole truth, but it seems to me that there is truth in it and that it is a distinct step, and the first that has been taken to bring the vast number of inorganic compounds (and perhaps organic as well) in one category, to unify our science. It is in its present form crude, as with most new theories ; much remains to be done. The multifarious classes of complex compounds must be studied in their relation to the theory and relegated to their proper type, and these types must be studied in their relation to the periodic system. I cannot better close this imperfect review than by quoting from Werner : "The modern doctrine of the constitution of chemical compounds, worked out in such a wonderful way, the doctrine of the inner structure of the molecule, is based upon a knowledge of the valence of the elements, and hence has taken a characteristic trend. It is the doctrine of the constitution of valence compounds. In unfortunate contrast to the thorough development of this, stands the development of the doctrine of the constitution of molecular compounds; and this is the case chiefly because the idea of valence fails when applied to these compounds. Practically, the only molecular compounds of which the modern doctrine of chemical constitution takes cognizance, are those for which, by the help of lines and 'bonds,' a meager and questionable valence formula can be pictured." Let us hope that the near future will give us a broader view.

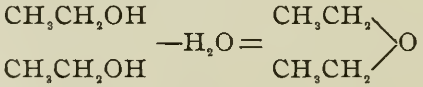
JAS. LEWIS HOWE.

References to Werner's Theory of the Constitution of Inorganic Compounds.

Ztschr. anorg. Chem., **3**, 267; **5**, 147; **7**, 108, 289; **8**, 153, 189; **9**, 382; **10**, 320; **11**, 254, 416; **13**, 172, 211; **14**, 21, 263, 367, 404; **15**, 1, 123, 143, 243; **16**, 109, 244, 377, 398; **17**, 35, 82, 480; **18**, 152, 253; **19**, 106, 109, 158; **21**, 96, 145. Ber. d. chem. Ges., **28**, 1489, 1493.

SCHOOL CHEMISTRY. BY CHARLES BASKERVILLE, PH.D., The University of North Carolina. Richmond, Virginia: B. F. Johnson Publishing Co. 1899. 159 pages.

In the preface the author says "The material * * * has been adapted to the needs of the schools in the Southern States." "A large part of the ninety per cent of high school graduates, who do not secure a college or university training, never learn a chemical principle or fact except by accident. The course presented is not intended to replace college work, but seeks that class of people mentioned." The author has fallen into the error, which is so common in books of this kind, of trying to cover the whole field in a few lessons. Would it not be far better to study a few typical substances thoroughly, rather than to have one thing after another mentioned in a brief unsatisfactory way. The theoretical part, as it must necessarily be in such a work, is a mere statement of facts which cannot make the desired impression without a clear presentation of the reasons upon which the deductions are based. The atomic theory is explained (?) in about a dozen lines in the early part of the book, while the laws of definite and multiple proportions are not mentioned until much later. What impression does it make on one who has only had twenty lessons when he is told that if "we subtract a molecule of water from two molecules of alcohol, we have



$$\begin{matrix}\mathrm{CH_3CH_2OH}\\ \mathrm{CH_3CH_2OH}\end{matrix}\ -\mathrm{H_2O}=\ \begin{matrix}\mathrm{CH_3CH_2}\\ \mathrm{CH_3CH_2}\end{matrix}\!\Big\rangle\mathrm{O}$$

a body called an ether." "Sulphuric acid has the power of tearing water away from certain substances, hence we may use that reagent for removing water from alcohol to produce ether."

The author says that this book is the outcome of five years' experience as a teacher in a summer school for teachers. It is an unfortunate system which necessitates such books as compendiums and condensed works for those who imagine they can successfully complete a year's work in a few weeks.

J. E. G.

DIE LEHRE VON DER ELEKTRIZATÄT. BY GUSTAV WIEDEMANN. Second, revised and enlarged, edition. Vol. IV. Large 8vo. xiii + 1237 pp. Braunschweig: F. Vieweg & Sohn, 1898. Price, 32 marks.

It is very fortunate that the fourth and concluding volume of Wiedemann's great handbook of electricity was completed before the author's recent death. The volume treats induction, the absolute measure of electrical quantities, and the hypothetical views that have been held regarding electricity and its mode of action. But little of this has a direct bearing upon chemistry. The chief items of interest are, probably, the reports upon the resistance offered by electrolytes to currents induced by electric waves; and upon the relation between chemical composition and dielectric constant, as studied by Thwing, Landolt and John, Nernst, Drude, and others. The concluding chapter has, of course, an interest for the general reader. It is announced that a subsidiary volume, by Eilhard Wiedemann, will be devoted to the conduction of electricity by gases. J. E. T.

THE ELEMENTS OF BLOWPIPE ANALYSIS. BY F. H. GETMAN, F. C. S., Instructor in Chemistry in the Stamford High School. New York: The Macmillan Co. 1899. 77 pages. 60 cents.

This book is intended for use in high schools and colleges and is designed to give the student a general outline of blowpipe analysis, and to introduce him to the methods of determinative mineralogy. The material has been simplified as much as possible and tables for 'systematic' examination have been omitted. After describing the methods of work, the author takes up each element in turn and gives its behavior, or leaves it blank to be filled out by the student, when heated alone on platinum wire or with various reagents. The reactions of some of the principal ores are also given. J. E.G.

LABORATORY MANUAL. Experiments to Illustrate the Elementary Principles of Chemistry. BY H. W. HILLYER, PH.D., Assistant Professor of Organic Chemistry in the University of Wisconsin. New York. The Macmillan Co. 1899. 200 pages. 90 cents.

This book can be highly recommended as a laboratory guide for those beginning the study of chemistry. The experiments are arranged in a logical order and are very clearly presented. The student is not, as is so often the case, compelled to go far beyond his depth at the first step, but he feels his way slowly and carefully, getting a firm foundation from a thorough study of a few of the simpler elements before taking up more difficult problems. For those students who, from a course in some preparatory school, are in a position where it would be unprofitable to follow the exact course designed for beginners, and who, on the other hand, are not fitted to pursue a more advanced course, the author has introduced some supplementary experiments throughout the book and also some simple quantitative experiments. The experiments are printed on only one side of the page, the other being blank for the results of the experiments. J. E. G.

THE NEWER REMEDIES. BY VIRGIL COBLENTZ, A.M., Phar.M., Ph.D., F.C.S., Etc., Professor of Chemistry and Physics in the New York College of Pharmacy. Third Edition. Philadelphia: P. Blakiston's Son & Co. 1899. Price, $1.00.

Questions concerning the composition and properties of the new remedies, which are almost daily introduced, are constantly being put to the chemist and the pharmacist, and frequently they cannot answer them, as it is impossible to keep thoroughly informed on the subject. In most cases no idea of the composition can be obtained from the name, and when we consider that about 1200 of these remedies have been introduced in the last three years, the hopelessness of the problem is better realized. The author has come to our aid with this book, in which he has collected several thousand of the new remedies arranged in alphabetical order with the methods of preparation, tests, solubilities, doses, and other properties which may be of interest. It is a valuable reference book on this subject, and is published in a handy and neat form. J. E. G.

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Contribution from the Laboratory of General Chemistry of the University of Michigan.

THE RATE OF ACTION OF WATER ON CERTAIN α- β- AND γ-HALOGEN SUBSTITUTED FATTY ACIDS.

BY EDWIN DEBARR.

In the course of the investigations which were undertaken for the purpose of ascertaining the initial rate and limit of esterification of the halogen substituted fatty acids, it became evident that a study of the decomposition of these same substances by water was also necessary, with the object of fixing the lowest limit at which the change sets in. In following out this line, the necessity also soon showed itself of applying methods to this phase of the investigation similar to those developed in the study of esterification,[1] so that the research has practically changed into a determination of the velocity of the action of water on the substances in question.

The following acids came within the scope of the research: monochloracetic, dichloracetic, trichloracetic, α- and β-chlorpropionic, α-brompropionic, α-brombutyric, α-, β-, and γ-chlorbutyric, the object in treating the β- and γ-acids being to ascertain the influence of the distance of the halogen atoms from the carboxyl group, and in the case of the γ-acid, the effect of the tendency to form lactones displayed by the corresponding oxy-acid, which would be produced by hydrolysis.

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[1] Lichty: This JOURNAL, 18, 590 (1896); Menschutkin: Ber d. chem. Ges., 11, 1507.

During the course of the work it became necessary to somewhat modify the former methods of preparation of some of the substances investigated, the result being that in certain instances new boiling- and melting-points were observed for the absolutely pure products. The instances in which such modified methods were used are given below.

EXPERIMENTAL PART.

Preparation of β-Chlorpropionic Acid.

The β-chlorpropionic acid used in this investigation was prepared from β-iodopropionic acid,[1] the latter formed by a slight modification of the method of Victor Meyer.[2] In order to convert this product into pure β-chlorpropionic acid and obtain a good yield, it is essential to adhere closely to the following directions:

β-Iodopropionic acid is dissolved in almost ten times its own weight of water and chlorine is slowly passed in, the current being stopped from time to time and the contents of the flask thoroughly shaken until the odor of chlorine entirely disappears. The operation is complete when the gain in weight equals that required by theory. The iodine is then filtered off, the solution treated with sulphur dioxide until colorless, and then repeatedly extracted with ether.

After drying over calcium chloride and evaporating the solvent, the remainder is distilled several times over molecular silver, when all but a small trace of iodine is removed. The absolutely pure acid is then obtained by repeated recrystallization from ligroin. Its melting-point is 61°; its boiling-point is 204°; the previous melting-points[3] have been given from 35°.5–58°.

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[1] Erlenmeyer: Ann. Chem. (Liebig), **191**, 284; Rosenthal: *Ibid*, **233**, 16 (1886); V. Meyer: Ber. d. chem. Ges., **19**, 3294; **21**, 24.

[2] The iodide of phosphorus is best made by dissolving 6.5 grams of yellow phosphorus in carbon disulphide and then slowly adding 50 grams of iodine, allowing to crystallize, and evaporating the carbon bisulphide in a vacuum. Pure garnet-red crystals, entirely free from iodine, are thus obtained, with the result that the subsequent addition of glyceric acid allows the reaction to go much more smoothly.

[3] Henry: J. prakt. Chem. [2], **31**, 127.

Preparation of β-Chlorbutyric Acid.

β-Chlorbutyric[1] acid was prepared by saturating an ethereal solution of crotonic acid with hydrochloric acid gas at 0°, sealing in a tube, and then allowing to stand at the temperature of the room for twenty-four hours. The tube was then opened, the ether evaporated, and the remainder dried in a desiccator, over lime and sulphuric acid, the final product being distilled at 22 mm. pressure, the boiling-point being 116°. On analysis this substance was found to be pure β-chlorbutyric acid, melting at 16°–16°.5.[2] [3]

Preparation of γ-Chlorbutyric Acid.

γ-Chlorbutyric[4] acid was made by saturating at 0°, with hydrochloric acid, an ethereal solution of trimethylenemonocarboxylic acid, placed in a tube which was sealed and allowed to stand forty-eight hours at the temperature of the room. At the end of this time the tube was opened, the ether evaporated, and the contents dried in a desiccator over lime and sulphuric acid, after which the residue was fractioned under diminished pressure, when it boiled at 196° (22 mm.).

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[1] Karetnikow: J. Russ. Soc., **11**, 252; Pinner: Ber. d. chem. Ges., **12**, 2056; **17**, 2008; Michael and Freer: J. prakt. Chem. [2], **40**, 95 (1889).

[2] The crotonic acid used in preparing the β-chlorbutyric acid was made according to the following method: 10 grams of acetoacetic ester are dissolved in 250 cc. of water, placed in an Erlenmeyer flask, and surrounded by ice-water, 10 such flasks being treated at the same time. To each, gradually, soft or liquid sodium amalgam is added and then, from time to time, glacial acetic acid from a burette so that the solution at no time has other than a slightly alkaline reaction (a decided alkalinity or acidity is to be guarded against). When hydrogen passes through the mixture freely, the mercury is filtered, the whole acidified with concentrated sulphuric acid, and then distilled with steam. At first acetic acid, then oxybutyric acid, and finally, after continuing the operation for some time, crotonic acid comes over. All the distillates containing crotonic acid are shaken out with ether, the ether dried over calcium chloride, and evaporated, the acid being purified by recrystallizing it from ether. The distillates containing oxybutyric acid are neutralized with calcium carbonate and evaporated to dryness on a water-bath; concentrated sulphuric acid is then added to the calcium oxybutyrate, and the latter again distilled with superheated steam, by which means a further quantity of crotonic acid can be isolated. In this manner 40 grams of crotonic acid were obtained from 100 grams of acetoacetic ester.

[3] The absence of α-acid was proved by decomposing the β-chlor acid by carefully boiling with aqueous potash, added gradually until the solution was permanently alkaline. It was then acidified, extracted with ether, the solution dried, and the solvent evaporated. Almost all of the remainder crystallized to *crotonic acid* (m. p. 71°), the crystals were filtered off by a filter-pump, and the remaining syrup boiled with zinc carbonate, filtered, and evaporated. The zinc salt was entirely amorphous, demonstrating the absence of α-oxybutyrate.

[4] Henry: Bull. Soc. Chim. (Paris), **45**, 341.

On analysis the substance was found to be pure γ-chlorbutyric acid, melting at 12°.

Method of Investigation.

At the outset it was necessary to determine the temperature at which water begins to act upon the chloracetic acids. This investigation was carried on in sealed tubes of from 5 to 8 cc. capacity. Approximately 0.1 gram of water was introduced into each of several thin-walled, glass bulbs of about 1 cc. capacity, and each was then sealed. One of these bulbs was inserted into a tube, a molecular amount of acid introduced, and the larger tube sealed by drawing to a thin point, the first set of determinations being made with 1 molecule of water to 1 molecule of monochloracetic acid. The small bulb on the inside was broken in each case by shaking, and the tube was then immediately immersed in a bath of boiling water, and heated for a given time. It was then rapidly cooled by dipping into vessels containing water of different degrees of temperature, after which the amount of acid changed was immediately estimated. It was found that below 110° there was practically no change with 1 molecule of water to 1 molecule of monochloracetic, α-chlorpropionic, or α-brombutyric acids.

In the study of di- and trichloracetic acids 2 and 3 molecules, respectively, of water were used, and, although decomposition took place more readily with these acids, it was, nevertheless, necessary to use a higher temperature with the others, so that all were finally decomposed at 150°. For this purpose a glycerine-bath of about 10 kilograms' capacity was employed, the various tubes being suspended therein while being heated. A gas-regulator consisting of a mercurial portion outside of the bath connected with a bulb of about 200 cc. capacity, submerged in the glycerin, was used, the gas being supplied to the mercurial portion from a gas-regulator of the pattern described by Murrill.[1] The tubes prepared for investigation, with the inside bulbs broken, were suspended by means of wires in the glycerin, and the time of their introduction noted. At no time during the investigation did the temperature fall below 149°, nor did it rise above 150°. The temperature was observed every fifteen minutes during the investigation of any acid.

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[1] J. Am. Chem. Soc., **20**, 501.

In every case, except trichloracetic acid, the amount of acid transformed was estimated by a tenth-normal solution of silver nitrate with yellow potassium chromate as indicator, the free organic acid as well as the hydrochloric acid being removed by sodium or potassium acetate.

When the proper time came for taking out any tube, it was dipped into boiling, then hot, then warm, and finally into cold water. The small point was broken off under water in the vessel in which the estimation of hydrochloric acid was to be made, and the amount of the latter substance determined as soon as possible.

In the case of trichloracetic acid a variation from the above-mentioned method was resorted to, for the amount decomposed was estimated by difference, the determination of the acid not transformed being by use of a tenth-normal solution of barium hydroxide with methyl orange or phenolphthalein as indicator.

Results Obtained with Monochloracetic Acid at 150°.

The following results were obtained with 1 molecule of water and 1 molecule of monochloracetic acid at 150° C.

Time in hours.	Per cent of acid transformed.
½	1.01
1	1.74
2	2.01
3	3.77
4	5.45
5	5.72
6	5.87
7	6.90
8	7.37
9	7.44
10	7.65
15	19.65
20	24.41
30	20.76

After thirty hours the tubes, on being opened, began to show pressure and the contents became dark, the amount of acid apparently transformed being then less than at twenty hours, showing that by-products were being formed which absorbed hydrochloric acid and altered the nature of the reaction. As the amount of hydrolysis was limited when only 1 molecule of each substance was heated, it was necessarily decided to investigate the rate of action of 2 molecules of water to 1 molecule of monochloracetic acid, and the following results were obtained :

Time in hours.	Per cent of acid transformed.
1	6.08
2	9.71
3	12.60
4	14.24
5	13.58
6	18.83
7	10.27
8	26.28
9	28.35
10	28.20
15	36.38
20	44.33

At the end of twenty-four hours the tubes showed pressure. This amount of water did not give the results hoped for. The investigation was changed, 3 molecules of water being used to 1 molecule of monochloracetic acid. The results are given in the following table : (See Figure 1.)[1]

Time in hours.	Per cent of acid transformed.	Average per cent.
$\frac{1}{2}$	3.98	4.06
	4.14	
1	8.63	8.59
1	8.55	
2	15.78	14.46
2	13.13	
3	25.26	25.23
3	25.19	
4	29.76	29.30
4	28.83	
5	34.39	33.89
5	33.39	
6	36.80	36.90
6	37.00	

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[1] In all the figures except 3 the curves are drawn on the basis of time in hours.

Time in hours.	Per cent of acid transformed.	Average per cent.
7	40.70	40.71
7	40.71	
8	41.00	41.10
8	41.20	
9	41.08	41.20
9	41.31	
10	41.31	41.32
10	41.32	
15	41.29	41.33
15	41.36	
20	43.93	43.85
20	43.78	
24	46.07	46.50
24	46.92	
30	47.03	47.03
30	47.03	

The tubes that were heated more than thirty hours exhibited pressure. Owing to these results and for the sake of comparison it was now decided to treat 1 molecule of each acid with 3 molecules of water for each chlorine atom present.

Rate of Action of Dichloracetic Acid and Water at 150°.

Dichloracetic acid was heated with 6 molecules of water to 1 molecule of the acid, and the following results were obtained: (See Figure 2.)

Time in hours.	Per cent of acid transformed.	Average per cent.
½	5.31	5.32
½	5.33	
1	7.91	7.93
1	7.94	
2	12.16	12.17
2	12.17	
3	13.61	13.52
3	13.43	
4	15.88	16.01
4	16.21	
5	17.80	17.76
5	17.71	

The tubes that were heated for six hours gave evidence of pressure when they were opened.

Dichloracetic acid was also heated with 8, 10, 12, and 18 molecules of water, respectively, to 1 molecule of the acid. In each case carbon was set free and the tubes exhibited pressure in less than ten hours.

One feature of interest presented itself here as well as in the case of the monochloracetic acid. The size of the tube as compared with the amount of the acid used seemed to affect the amount of transposition, for the duplicates containing the smaller amount of acid in proportion to the size of the tubes always gave the higher result.

Rate of Action of Water with Trichloracetic Acid at 150° C.

One molecule of trichloracetic acid was heated with 9 molecules of water with the following results: (See Figures 3 and 4.)

Time.	Per cent of acid transformed.	Average per cent.
5 min.	6.41	6.33
5 “	6.24	
10 “	13.20	13.45
10 “	13.70	
15 “	22.80	22.80
15 “	22.79	
20 “	27.67	27.68
20 “	27.68	
24 “	31.74	31.74
24 “	31.74	
30 “	42.50	42.38
30 “	42.25	
45 “	51.60	51.85
45 “	52.10	
1 hr.	79.83	79.92
1 “	80.01	
1¼ hrs.	92.34	92.23
1¼ “	92.11	
1½ “	92.24	92.67
1½ “	93.10	
1¾ “	95.23	95.30
1¾ “	95.36	
2 “	96.26	96.18
2 “	96.10	
3 “	97.20	97.21
3 “	97.22	
4 “	98.54	98.54
4 “	98.54	

Time.	Per cent of acid transformed.	Average per cent.
5 hrs.	98.60	98.60
5 “	98.60	
6 “	98.70	98.75
6 “	98.80	
7 “	99.40	99.40
7 “	99.39	
8 “	100.00	100.00
8 “	100.00	

Rate of Action of α-Chlorpropionic Acid with Water at 150° C.

One molecule of α-chlorpropionic acid was heated with 3 molecules of water and the following results were obtained: (See Figure 5.)

Time.	Per cent of acid transformed.	Average per cent.
½ hr.	4.45	4.42
½ “	4.39	
1 “	6.21	6.22
1 “	6.23	
2 hrs.	8.98	8.70
2 “	8.42	
3 “	11.97	11.41
3 “	10.84	

Tubes heated longer than three hours showed pressure.

Rate of Action of α-Brompropionic Acid with Water at 150° C.

α-Brompropionic acid was heated with 3 molecules of water with the following results: (See Figure 6.)

Time.	Per cent of acid transformed.	Average per cent.
½ hr.	2.89	2.93
½ “	2.97	
1 “	5.29	5.31
1 “	5.33	
2 hrs.	7.13	7.06
2 “	6.99	

Tubes heated longer than two hours showed pressure.

Rate of Action of α-Chlorbutyric Acid with Water.

α-Chlorbutyric acid was heated with 3 molecules of water with the following results: (See Figure 7.)

Time.	Per cent of acid transformed.	Average per cent.
¼ hr.	1.80	1.90
¼ "	2.00	
½ "	5.80	5.80
½ "	5.80	
1 "	6.40	6.50
1 "	6.60	
2 hrs.	7.01	7.02
2 "	7.03	
3 "	7.50	7.50
3 "	7.50	

The tubes that were heated longer than three hours gave evidence of pressure.

Rate of Action of α-Brombutyric Acid with Water at 150° C.

α-Brombutyric acid was heated with 3 molecules of water and the following results were obtained: (See Figure 8.)

Time.	Per cent of acid transformed.	Average per cent.
½ hr.	3.76	3.77
½ "	3.77	
1 "	5.78	5.80
1 "	5.81	
2 hrs.	7.29	7.27
2 "	7.24	
3 "	9.24	9.25
3 "	9.26	

The tubes which were heated more than three hours gave evidence of pressure.

Rate of Action of β-Chlorpropionic Acid with Water at 150° C.

β-Chlorpropionic acid was heated with 3 molecules of water to 1 of acid and the following results were obtained: (See Figure 9.)

Time.	Per cent of acid transformed.	Average per cent.
5 min.	18.21	18.26
5 "	18.30	
10 "	23.00	23.23
10 "	23.46	
15 "	39.97	40.44
15 "	40.90	
30 "	41.30	41.50
30 "	41.70	

Time.	Per cent of acid transformed.	Average per cent.
1 hr.	43.71	43.57
1 “	43.42	
2 hrs.	47.16	47.33
2 “	47.50	
3 “	49.25	49.44
3 “	49.63	
4 “	50.16	50.49
4 “	50.81	

Tubes that were heated more than four hours gave evidence of pressure.

Rate of Action of β-Chlorbutyric Acid with Water at 150° C.

Three molecules of water were heated with 1 molecule of β-chlorbutyric acid with the following results: (See Figure 10.)

Time.	Per cent of acid transformed.	Average per cent.
2 min.	1.52	1.92
2 “	2.32	
5 “	2.65	2.41
5 “	2.17	
10 “	4.15	4.22
10 “	4.29	
15 “	12.48	12.74
15 “	13.00	
30 “	30.29	29.97
30 “	29.65	
1 hr.	35.50	35.70
1 “	35.90	
2 hrs.	36.46	36.96
2 “	37.45	
3 “	37.36	37.38
3 “	37.40	

Tubes that were heated longer than three hours gave evidence of pressure.

Rate of Action of γ-Chlorbutyric Acid with Water at 150° C.

When γ-chlorbutyric acid is heated with 3 molecules of water to 1 of the acid the transformation is complete in five minutes, the action being so rapid that the curve showing the rate cannot be determined with any degree of accuracy.

The effect produced by the varying size of the tubes to which attention was called under the heads of mono- and dichloracetic acids was noticed throughout the work with the other acids, for the duplicate having the larger capacity with a proportionally smaller amount of acid invariably gave the higher figures, while these tubes which were of the same capacity and contained the same amount of acid invariably gave concordant results. In all instances the external conditions were absolutely unvarying ; the differences could therefore only be due to the variations in the size of the tubes. In the tables the duplicate result represents that with the larger tube.

Comparison of Results.

We find, by comparing the rates of action of the various acids with water, the following results :

Acid.	Per cent of transformation. One-half hour.	One hour.
Monochloracetic	4.06	8.59
Dichloracetic	5.32	7.93
Trichloracetic	42.38	79.92
α-Chlorpropionic	4.42	6.22
α-Brompropionic	2.93	5.31
α-Brombutyric	3.77	5.80
α-Chlorbutyric	5.80	6.50
β-Chlorpropionic	41.50	41.50
β-Chlorbutyric	29.97	35.70
γ-Chlorbutyric	100.00	100.00

Acid.	Per cent of transformation.	Time transformation ceases.
Monochloracetic	47.11	30 Hrs.
Dichloracetic	17.76	5 "
Trichloracetic	100.00	8 "
α-Chlorpropionic	11.41	3 "
α-Brompropionic	7.06	2 "
α-Brombutyric	9.25	3 "
α-Chlorbutyric	7.50	3 "
β-Chlorpropionic	50.49	4 "
β-Chlorbutyric	37.38	3 "
γ-Chlorbutyric	100.00	5 Min.

The lowest limit at which the regular run of the reaction ceases and at which decomposition sets in is to be found with α-brompropionic acid. So that, for purposes of comparison, it is perhaps best to construct a table showing the time limit at which, in each case, 7 per cent has been transposed. The results are as follows :

	Acid.	7 per cent.	18 per cent.
1	γ-Chlorbutyric	Few sec.	Few sec.
2	β-Chlorpropionic	1 min.	5 Min.
3	Trichloracetic	6 "	12 "
4	β-Chlorbutyric	11 "	20 "
5	Monochloracetic	45 "	30 "
6	Dichloracetic	60 "	
7	α-Chlorpropionic	75 "	
8	α-Brompropionic	120 "	
9	α-Brombutyric	120 "	
10	α-Chlorbutyric	120 "	

Based upon this table, the order of affinity for the above acids would be :

1 γ-Chlorbutyric acid.
2 β-Chlorpropionic acid.
3 Trichloracetic acid.
4 β-Chlorbutyric acid.
5 Monochloracetic acid.
6 Dichloracetic acid.
7 α-Chlorpropionic acid.
8 α-Brompropionic acid.
9 α-Brombutyric acid.
10 α-Chlorbutyric acid.

The affinity constants of these acids,[1] so far as they have been determined, are as follows :

Acid.	K.
Acetic	0.0018
Monochloracetic	0.155
Dichloracetic	5.1
Trichloracetic	121.0
α-Brompropionic	0.108
β-Brompropionic	0.0098
α-Brombutyric	0.106

So that the order in which decomposition takes place is, excepting in the cases of mono-, di-, and trichloracetic acids, not the same as is that of the affinity constants.

The acids begin to break down, giving pressure in the tubes, when the following per cents have entered into reaction :

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[1] Walden : Ztschr. phys. Chem., **10**, 563, 638.

Acid.	Per cents.	Time.
α-Brompropionic	7.06	2 hrs.
α-Chlorbutyric	7.50	3 "
α-Brombutyric	9.25	3 "
α-Chlorpropionic	11.41	3 "
Dichloracetic	17.76	5 "
β-Chlorbutyric	37.38	3 "
Monochloracetic	47.11	30 "
β-Chlorpropionic	50.49	4 "
Trichloracetic	100.00	8 "
γ-Chlorbutyric	100.00	5 min.

This is then the stability of the compounds at 150°, under pressure and in the presence of hydrochloric acid. The interesting fact is then developed that the order of stability is the same as that of the affinity. In other words, the acids which are most stable react the most rapidly, and those which are least stable react the most slowly.

The time limit of the transposition of the various acids is affected by the number of carbon atoms in 1 molecule in the respective acids, so that the time becomes markedly less in passing from the derivatives of acetic acid to the next higher homologues. This is especially apparent with the α-monochlor acids. Thus chloracetic acid reaches its limit in thirty hours, α-chlorpropionic in three hours, and α-chlorbutyric acid in three hours.

Examining the β-acids we find that β-chlorpropionic acid reaches its limit in four hours, while β-chlorbutyric acid does so in three hours, a result similar to that observed with the α-acids.

We have observed no other γ-acid with which to make a comparison. We need not take the limit to make these comparisons, but if we observe the transformation of the various acids at the end of one hour, the same observations are true as to amounts. The greater the number of carbon atoms in the α-acids passing from acetic acid to the next higher homologues the less is the amount of acid transformed at the end of one hour. The same law holds true in the case of the β-acids.

In discussing the influence of distance of halogen from the carboxyl group, the most interesting fact is that the rate of transposition rapidly increases, the further the halogen atom, in any given molecule, is, according to our present views, removed from the carboxyl group. This is notably the case with α-chlorpropionic (4.42 per cent after one-half hour) and β-chlorpropionic acids (41.5 per cent after one-half hour) and with α-brombutyric (3.77 per cent), β-chlorbutyric (29.97 per cent), and γ-chlorbutyric acids (100 per cent). This result would not be surprising with γ-acids, as the tendency to form lactones would there play a prominent part, but this same reason cannot be alleged in the case of the β-acids, where there is an equally marked increase. So far as the work has gone, therefore, it would seem that the further a halogen atom is removed from the carboxyl group, the greater the influence of the latter on its reactivity, or, to put the matter in a different form, the protective action of the carboxyl group, if it exists, diminishes as the distance of the halogen, according to our present views, increases. It would be interesting to follow the influence also, in the cases of δ- and ω-acids, but the difficulty of preparing the latter in the pure state has hitherto stood in the way; the investigation will, however, be continued along this line.

So far, none of the reactions given above have been capable of being reduced to mathematical formulæ, and, indeed, more data are required before this can be successfully accomplished. Work on the esterification of these acids, as well as on the affinity constant, is now being conducted in this laboratory, with the ultimate object of combining all results so as to be able, if possible, to determine accurately the meaning of the term distance of the halogen from the carboxyl group.

The only previous work along these lines was done by Schwab,[1] who investigated the action of sodium hydroxide solution on monochloracetic acid in such a way that, while the amount of alkali remained constant, the solvent water was increased; it developed that the rate became greater as the amount of water increased, so that the rate depended upon the ionization of the acid. If this is true with monochloracetic acid, the cause of the differing reactive velocities noted alone may also be found in the degree of ionization. This question will be settled by the determination of the affinity constants.

[1] Schwab: Inaugural dissertation, Amsterdam, 1883.

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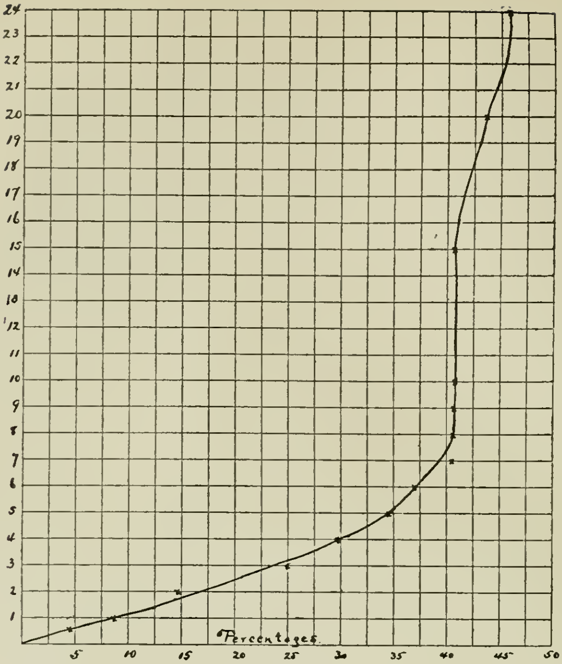

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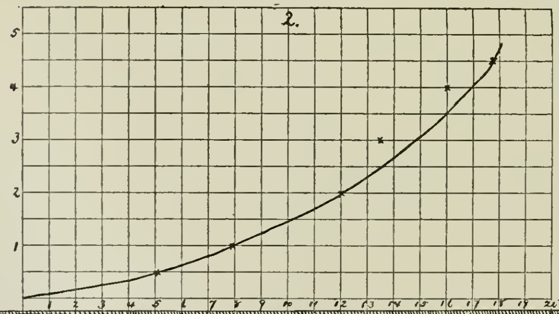

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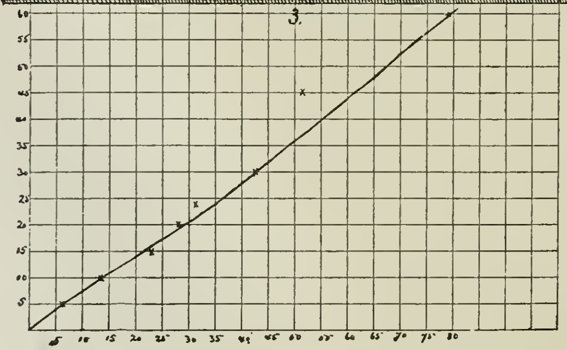

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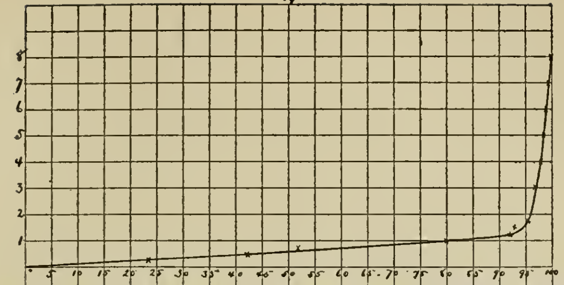
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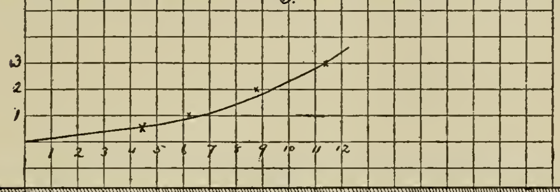
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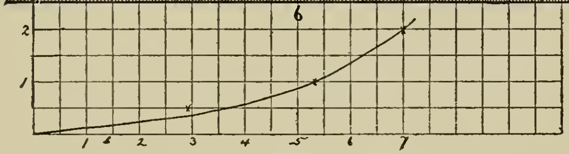
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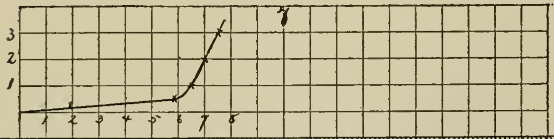
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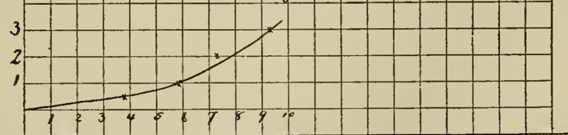
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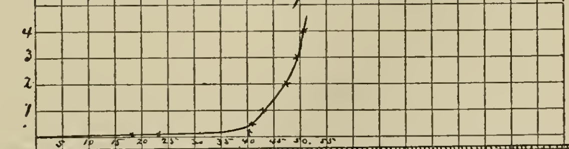
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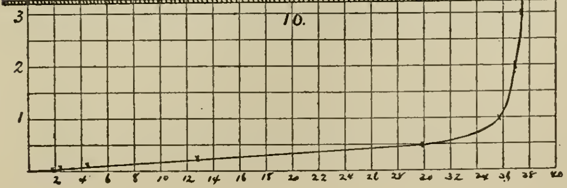
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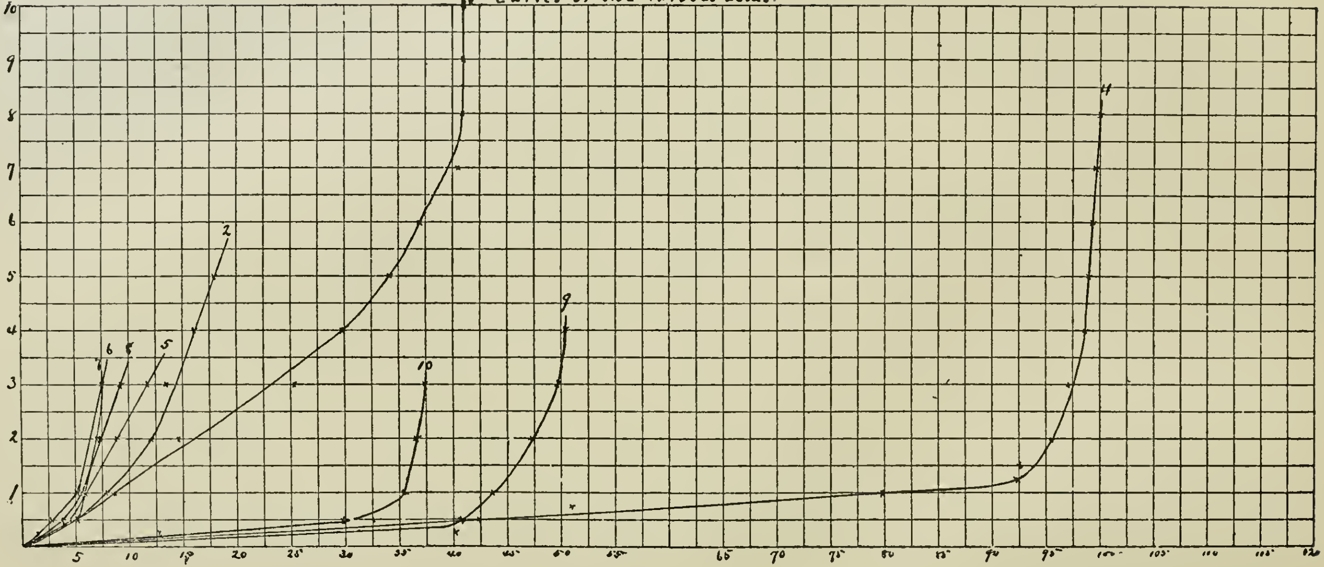
Curves of the various acids.



Contributions from the Chemical Laboratory of Harvard College.

CXV.—THE OCCLUSION OF HYDROGEN BY METALLIC COBALT AND OTHER METALS.[1]

BY GREGORY PAUL BAXTER.

In the course of the work upon the atomic weight of cobalt, described in preceding papers from this laboratory,[2] it became necessary to weigh metallic cobalt which had been reduced from the bromide and from the oxide by means of hydrogen. A few experiments were made at the time to show that the metal in question did not occlude appreciable amounts of hydrogen, but the comparison of this result with the conflicting accounts of others showed that the subject was worthy of further attention.

Hempel and Thiele,[3] by quantitative combustion of metal reduced from the oxide at a high temperature, obtained no water. Neumann and Streintz,[4] on the other hand, also working with material obtained from the oxide, found that their cobalt occluded in one case 150 times, in another 50 times, its volume of hydrogen. Troost and Hautefeuille[5] determined the occluded hydrogen by heating the metal in a vacuum and measuring the gas evolved. Ingots of cobalt, after ignition in hydrogen, yielded only 0.1 their volume of occluded gas; foil obtained by electrolysis evolved 35 volumes of hydrogen, and upon heating in hydrogen was found to have taken up 24 volumes, while powdery cobalt, obtained by reduction of the oxide, evolved 100 times its volume of hydrogen. This latter preparation proved to be pyrophoric in air, even after the hydrogen had been removed. Neumann and Streintz also observed the same property in their cobalt when exposed to an atmosphere of oxygen.

Although this evidence seems contradictory at first sight, in reality much can be said on both sides. Metallic cobalt shows widely different characteristics in its behavior toward hydrogen according to its purity and the method by which it is prepared. In some cases the present work shows it to have occluded only traces of hydrogen or none at all; in others it occluded amounts comparable with those found by Neumann and Streintz, and Troost and Hautefeuille.

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[1] The investigation on the atomic weight of cobalt, of which this paper formed a part, was presented to the Faculty of Arts and Sciences of Harvard University as a thesis for the degree of Ph.D., in 1899.

[2] Richards and Baxter: Proc. Amer. Acad., **33**, 115 (1897); **34**, 351 (1899); **35**, 61 (1899).

[3] Zeit. anorg. Chem., **11**, 93.

[4] Monatsh. Chem., **12**, 642.

[5] Compt. rend., 80, 788.

In the following experiments the occluded hydrogen was determined by the method already mentioned;—combustion of the metal and determination of the water formed. For this purpose the following apparatus was used:

Three columns of beads moistened with strong sulphuric acid were followed by a tube containing phosphoric anhydride. These were connected with a combustion tube which contained the boat with the metal under examination and beyond the boat a coil of copper oxide. This copper oxide was prepared by igniting a roll of copper gauze in oxygen. Beyond this apparatus was a weighed phosphoric pentoxide tube, and this in turn was connected with an aspirator through an unweighed safety drying tube.

Owing to the fact that the organic matter emanating from rubber upon combustion will yield water, rubber was wholly avoided in this apparatus with the exception of the connections necessary for making attachment to the combustion tube. All other joints were made wholly of glass.

After the introduction of the boat containing the cobalt into the combustion tube, and before the absorption bulb was attached, a slow current of air was drawn through the tube for some time, while the copper oxide was heated to dull redness. The weighed bulb was then inserted in the circuit and the section of the tube containing the boat was heated until oxidation of the metal took place. In order to avoid removal of oxygen from the air which should finally fill the absorption bulb, the current of air was continued until the boat had become cool.

After each analysis the phosphoric anhydride bulb, which could be closed by means of glass stop-cocks, was wiped with a damp cloth and allowed to stand in the balance-case one-half hour. Needless to say, before the bulb was weighed the pressure inside and out was equalized by opening one of the stop-cocks. As the time between two successive weighings was never more than two hours and usually not more than one, atmospheric conditions did not change sufficiently to necessitate weighing the bulb by substitution, so this precaution was omitted.

Several blank experiments were carried out in which the average gain in weight of the bulb per hour was 0.2 gram. In another case a tube, the volume of which was 13.0 cc., filled with pure hydrogen at the room temperature, was inserted in the apparatus and the water formed by the combustion of the hydrogen was collected in the bulb. The weight of the water formed in two experiments was 0.0111 gram and 0.0107 gram, while theory required 0.0108 gram. Evidently the apparatus was effective for its purpose.

In several instances which have already been described,[1] pure cobalt reduced from the bromide was heated to 500° in a hard glass tube, from which the air had previously been completely exhausted by a Sprengel air-pump. In no case was a measurable quantity of gas evolved and the cobalt did not lose in weight. Although at the time the evidence seemed sufficient to show that this cobalt did not possess the property of occluding important amounts of hydrogen when heated in this gas, a few grams of metal reduced from the bromide were subjected to quantitative combustion. In calculating the volumes of occluded hydrogen given under the following analyses, the specific gravity of cobalt is assumed to be 8.5, and the weight of a liter of hydrogen, at 20° and 760 mm. pressure, to be 0.0839 gram.

I. 2.5 grams of cobalt yielded 0.0005 gram of water, or 2.0 volumes of hydrogen.

II. 2.5 grams of cobalt yielded 0.0010 gram of water, or 4.0 volumes of hydrogen.

III. 2.5 grams of cobalt yielded 0.0004 gram of water, or 1.6 volumes of hydrogen.

In analyses II and III the original cobalt was reduced and reoxidized, and it can be seen that this treatment produced no appreciable effect upon the amount of the occluded hydrogen. It was evident that cobalt reduced from the bromide does not possess the property of occluding hydrogen to an important extent.

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[1] Proc. Amer. Acad., 34, 355.

On the other hand, cobalt reduced originally from the oxide was found to contain amounts of hydrogen varying widely with the purity and the method of preparation. Cobalt oxide, free from alkalies and silica, was obtained by dissolving electrolytic metal in the purest nitric acid and precipitating the cobalt as hydroxide by the addition of pure redistilled ammonia, all in platinum vessels. No attempt was made to remove other impurities, since these could not have been present in sufficient quantities to produce an appreciable effect. This oxide was reduced in hydrogen at 400°–500°, and the metal was subjected to combustion as soon as cold. The weight of cobalt given is somewhat higher than it should be, owing to the fact that it is impossible to obtain complete reduction at the temperature employed. It will be shown later that a temperature sufficiently high to produce complete reduction alters the behavior of the metal toward hydrogen.

IV. 2.0 grams of cobalt yielded 0.0034 gram of water, or 19 volumes of hydrogen.

V. 6.4 grams of cobalt yielded 0.0105 gram of water, or 19 volumes of hydrogen.

VI. 2.9 grams of cobalt yielded 0.0053 gram of water, or 21 volumes of hydrogen.

As has already been suggested by Richards and Cushman,[1] the cause of this great difference in behavior might be explained by either of two hypotheses. The sodic bromide contained in the cobaltous bromide might be the agent which prevented the occlusion in the case of metal reduced from the bromide, or the volatility of the cobaltous bromide might allow the reduced metal to be deposited in a form essentially different from that reduced from the oxide. Two simple experiments served to decide this dilemma. In the first place the same 2.5 grams of cobalt reduced from the bromide were leached with pure water until all soluble matter had been removed. After drying and heating in hydrogen the metal was again subjected to combustion.

VII. 2.5 grams of cobalt yielded 0.0004 gram of water, or 1.6 volumes of hydrogen.

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[1] Proc. Amer. Acad., 34,333.

The first conception that the sodic bromide protected the reduced metal was evidently at fault. Furthermore, cobalt oxide that had been precipitated in the presence of much sodic chloride by means of sodic hydrate, and which consequently contained a large amount of alkaline and siliceous impurity, was reduced as usual with the intention of determining the effect of this alkali. Upon removing the boat containing the metal from the reduction tube spontaneous oxidation took place, and it was found necessary to replace the hydrogen in the reduction tube, after it was cool, by nitrogen and to insert the tube bodily between the drying train and the combustion tube. This cobalt differed from the samples previously examined in that it did not contract or "sinter" to any extent. Whether this effect was due to the alkalies or to silica is uncertain.[1] One determination of the hydrogen occluded by metal treated in this way was made.

VIII. 2.0 grams of cobalt yielded 0.0085 gram of water, or 48 volumes of hydrogen.

Evidently the impurities did not protect the cobalt from the hydrogen, hence one is driven to accept the second solution of the dilemma, and to decide that cobalt reduced from the bromide differs in its state from that obtained from the oxide.

The experiment already described of heating in a vacuum cobalt reduced from the bromide was now repeated with metal obtained from the oxide. In every case gas was evolved during this process, as would have been expected, and the metal upon combustion proved to contain only traces of hydrogen.

IX. 2.7 grams of cobalt yielded 0.0008 gram of water, or 3.5 volumes of hydrogen.

X. 5.0 grams of cobalt yielded 0.0010 gram of water, or 2.5 volumes of hydrogen.

XI. 5.0 grams of cobalt yielded 0.0014 gram of water, or 3.2 volumes of hydrogen.

That no appreciable amount of hydrogen was given off at ordinary temperatures was evident from the following analyses. The cobalt was placed in a hard glass tube, which was then exhausted, while cold, with a Sprengel air-pump. After this treatment it was subjected to combustion as usual (Analyses XII and XIII), and the oxide remaining from the combustion was again reduced and the metal analyzed for hydrogen as soon as cold (Analyses XIV and XV). It can be seen that the amounts of hydrogen obtained in the two cases are essentially the same.

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[1] Richards and Cushman found that nickel which had been "purified" in glass vessels contained enough of these two impurities to prevent its sintering when reduced in hydrogen (Proc. Amer. Acad., **34**, 328).

XII. 2.5 grams of cobalt yielded 0.0017 gram of water, or 7.6 volumes of hydrogen.

XIII. 2.7 grams of cobalt yielded 0.0035 gram of water, or 14.8 volumes of hydrogen.

XIV. 2.5 grams of cobalt yielded 0.0019 gram of water, or 8.6 volumes of hydrogen.

XV. 2.7 grams of cobalt yielded 0.0029 gram of water, or 12.3 volumes of hydrogen.

This was further shown by passing dry air first over cold freshly reduced metallic cobalt and then over hot copper oxide. The small amount of water formed was collected in the usual way, and is entirely in agreement with the preceding results.

XVI. 2.0 grams of cobalt yielded 0.0006 gram of water in one hundred and fifty minutes.

Troost and Hautefeuille, however, found that cobalt which contained one hundred times its volume of hydrogen gave up a considerable part of it in a vacuum without the application of heat.

In several analyses in which cobalt was allowed to stand in hydrogen for at least twenty-four hours at the room temperature, the amount of water obtained upon combustion was considerably larger than that obtained from metal which was subjected to combustion immediately after reduction.

XVII. 2.7 grams of cobalt yielded 0.0160 gram of water, or 68 volumes of hydrogen.

XVIII. 2.9 grams of cobalt yielded 0.0117 gram of water, or 46 volumes of hydrogen.

The metal of Analysis XVIII, when analyzed immediately after reduction, yielded 0.0053 gram of water.

In order to show that this difference was not due to a change in the metal itself (owing to the process of oxidation and reduction), equal amounts of the same preparation of oxide were reduced under conditions exactly similar. One sample (Analysis XIX) was allowed to stand in hydrogen at the room temperature for twenty-four hours; the other sample (Analysis XX) was subjected to combustion as soon as cold.

XIX. 2.3 grams of cobalt yielded 0.0043 gram of water, or 21 volumes of hydrogen.

XX. 2.3 grams of cobalt yielded 0.0022 gram of water, or 11 volumes of hydrogen.

From this fact that long-continued standing in cold hydrogen increases the amount of gas occluded, it is evident that cobalt possesses the property of taking up hydrogen at ordinary temperatures. This occlusion progresses only slowly in the cold, however, for the amount taken up in twenty-four hours was less than that occluded during ordinary reduction and cooling. In the following cases the metal was first heated in a vacuum and then allowed to stand in an atmosphere of hydrogen for twenty-four hours at the room temperature.

XXI. 2.7 grams of cobalt yielded 0.0020 gram of water, or 8.5 volumes of hydrogen.

XXII. 2.7 grams of cobalt yielded 0.0018 gram of water, or 7.5 volumes of hydrogen.

The same metal, after reduction and cooling in hydrogen, yielded 0.0035 gram of water.

Cobalt reduced in hydrogen and allowed to cool in pure nitrogen occluded only traces of hydrogen.

XXIII. 1.9 grams of cobalt yielded 0.0004 gram of water, or 2.1 volumes of hydrogen.

XXIV. 1.9 grams of cobalt yielded 0.0010 gram of water, or 5.4 volumes of hydrogen.

This same cobalt, when cooled in hydrogen, yielded 0.0029 gram of water upon combustion, or nearly 16 volumes of hydrogen.

According to Neumann and Streintz, repeated oxidation and reduction of the metal diminish its power of occluding hydrogen. From one sample they obtained first 150 volumes of hydrogen, then 50 volumes. Johnson, working with copper, noticed the same peculiarity, which is exhibited to a less striking extent by the metal used in the following two series of analyses:

XXV. 2.7 grams of cobalt yielded 0.0035 gram of water, or 14.8 volumes of hydrogen.

XXVI. 2.7 grams of cobalt yielded 0.0029 gram of water, or 12.3 volumes of hydrogen.

XXVII. 2.7 grams of cobalt yielded 0.0025 gram of water, or 10.5 volumes of hydrogen.

XXVIII. 2.7 grams of cobalt yielded 0.0035 gram of water, or 14.8 volumes of hydrogen.

XXIX. 2.7 grams of cobalt yielded 0.0025 gram of water, or 10.5 volumes of hydrogen.

XXX. 2.7 grams of cobalt yielded 0.0018 gram of water, or 7.5 volumes of hydrogen.

XXXI. 2.2 grams of cobalt yielded 0.0020 gram of water, or 10.2 volumes of hydrogen.

XXXII. 2.2 grams of cobalt yielded 0.0012 gram of water, or 6.2 volumes of hydrogen.

XXXIII. 2.2 grams of cobalt yielded 0.0019 gram of water, or 9.9 volumes of hydrogen.

XXXIV. 2.2 gram of cobalt yielded 0.0012 gram of water, or 6.2 volumes of hydrogen.

During the above process the metal gradually sintered together, occupying apparently much less volume than at first. If the same metal is then heated to redness in hydrogen it sinters much more still and yields only traces of hydrogen.

XXXV. 5.5 grams of cobalt yielded 0.0016 gram of water, or 3.5 volumes of hydrogen.

XXXVI. 6.2 grams of cobalt yielded 0.0004 gram of water, or 0.7 volume of hydrogen.

XXXVII. 2.5 grams of cobalt yielded 0.0003 gram of water, or 1.2 volumes of hydrogen.

Even impure oxide, obtained by igniting commercial nitrate, when heated to a high temperature in hydrogen, occluded only traces of this gas.

XXXVIII. 1.8 grams of cobalt yielded 0.0004 gram of water, or 2.5 volumes of hydrogen.

Metal reduced from impure oxide at low temperatures is not coherent but powdery, while pure metal shows a decided tendency to cling together. Pure metal reduced at high temperatures forms a hard solid mass. This sintering can be nothing more nor less than incipient fusion.[1] Where the minute particles of metal are in close contact with one another the contraction takes place very readily, while impurities keep apart the particles of metal and necessitate the application of higher temperatures to produce the same effect.

From the results of the work just described several important conclusions can be drawn. Cobalt in the form of ingots, which present a minimum amount of surface, is known to occlude almost no hydrogen. On the other hand, cobalt reduced from the oxide at a low temperature and consequently in a very finely divided condition offers a maximum amount of surface, and occludes relatively large amounts of hydrogen. Electrolytic foil, which, although it possesses considerable porosity, still lies between the above two modifications in relative surface, falls between them also in the amount of hydrogen retained. Neither Neumann and Streintz nor Troost and Hautefeuille took any precautions to purify their cobalt from alkalies or silica. Their metal, kept from sintering together by the impurities and the low reduction temperature, was in the finest state of division ; consequently it proved to be pyrophoric and to occlude maximum amounts of hydrogen, just as in Analysis VIII of this paper. That this property of spontaneous oxidation was not due to the hydrogen but to the large amount of surface presented to the air is shown by the fact that the metal used by Troost and Hautefeuille was still pyrophoric after it had been heated in a vacuum. The pure metal used in the work just described sintered considerably even at the lowest temperature at which reduction took place, and accordingly occluded much less hydrogen than the impure metal ; while even approximately pure metal when heated to a high temperature sintered together to such an extent that a minimum surface was presented to the hydrogen and only traces of this gas were occluded.

The first inference is perfectly clear. The volume of occluded hydrogen depends upon the amount of surface presented, which in the case of metals reduced from the oxide varies with the purity of the metal and the temperature of reduction.

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[1] Compare Richards : This JOURNAL, **20**, 725 (1898).

Again, since at ordinary temperatures the occlusion of hydrogen progresses very slowly (Analyses XXII and XXIII), while at the temperature of reduction, 400°–500°, it amounted to an almost negligible quantity (Analyses XXIV and XXV), at some intermediate temperature the occlusion must progress at a maximum rate.

Thirdly, the time during which the metal is in contact with the hydrogen is an important factor in determining the quantity of this gas taken up.

Finally, the volatility of cobaltous bromide evidently allows the metal reduced from it to be deposited in a form more compact and coherent than that reduced from the oxide, since the presence of sodic bromide was found to have no perceptible effect upon the amount of occluded gas.

The Occlusion of Hydrogen by Nickel.

The study of the occlusion of hydrogen was extended to the case of a few other metals. The behavior of nickel was found to be analogous to that of cobalt. According to Troost and Hautefeuille[1] nickel in the form of ingots retains only traces of hydrogen, metal reduced from the oxide occludes maximum amounts and is pyrophoric, while electrolytic foil occupies a position between the two. The amount of occluded gas, according to their results, was equal in quantity to that obtained from cobalt, 100 volumes in the case of metal reduced from the oxide. Raoult[2] states that very porous nickel, if used as the negative pole of a voltameter, takes up 165 volumes of hydrogen, the greater part of which is given off at ordinary temperatures in the air. These high results are contradicted by those of Neumann and Streintz,[3] who found about 17 volumes of gas in metal reduced from the oxide, and by those of Richards and Cushman,[4] who found only 8 volumes in the purest metal obtained from the same source.

The lesser values are supported by the following analyses performed with material kindly furnished by Dr. Cushman, and known to be free from every impurity. In Analyses I and II the nickel was subjected to combustion immediately after reduction. The oxide from Analysis I was reduced, and the resulting metal evolved no hydrogen in a vacuum, as was shown by the water yielded upon subsequent oxidation (Analyses III and IV). When heated in a vacuum the metal lost nearly all its occluded hydrogen (Analysis V). Like cobalt, nickel which had been heated to a high temperature during reduction sintered together and lost its power to occlude (Analysis VI). Finally, material reduced from the bromide occludes no hydrogen (Analysis VII), as has already been shown by Richards and Cushman.[1]

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[1] Compt. rend., **80**, 788.

[2] Jahresb., 1869, 272.

[3] Monatsh. Chem., **12**, 642.

[4] Proc. Amer. Acad., **34**, 333.

I. 5.7 gram of nickel yielded 0.0033 gram of water, or 5.7 volumes of hydrogen.

II. 4.0 grams of nickel yielded 0.0010 gram of water, or 2.1 volumes of hydrogen.

III. 5.7 grams of nickel yielded 0.0060 gram of water, or 10.7 volumes of hydrogen.

IV. 5.7 grams of nickel yielded 0.0057 gram of water, or 10.2 volumes of hydrogen.

V. 5.7 grams of nickel yielded 0.0017 gram of water, or 2.9 volumes of hydrogen.

VI. 6.0 grams of nickel yielded 0.0006 gram of water, or 1.0 volume of hydrogen.

VII. 1.5 grams of nickel yielded 0.0001 gram of water, or 0.7 volume of hydrogen.

Manifestly nickel is subject to the same influences as cobalt. The large amounts of hydrogen obtained by other experimenters can be explained by the fact that their material was very impure. Impure nickel and cobalt in the same state of minute subdivision apparently possess the property of retaining hydrogen to the same degree. Pure nickel, owing to its lower melting-point, should sinter more readily than pure cobalt. The lesser relative surface thus offered is probably the reason for the smaller amounts of occluded gas.

The Occlusion of Hydrogen by Copper.

The occlusion of hydrogen by copper has already been the subject of numerous researches which gave widely varying results.[1] One main fact stands out in all these investigations. Where the copper was known to be pure the occlusion was very slight, whatever the source of the copper.

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[1] Proc. Amer. Acad., 34, 333.

Very pure cupric oxide, made by evaporation of a solution of electrolytic copper in pure nitric acid, and ignition of the residue, after reduction yielded a very small amount of water (Analyses I, II, III, and IV). In a vacuum at ordinary temperatures the hydrogen was retained (Analysis 5), but after ignition in a vacuum a negligible amount of water was found (Analysis VI).

I. 2.5 grams of copper yielded 0.0003 gram of water, or 1.5 volumes of hydrogen.

II. 5.1 grams of copper yielded 0.0009 gram of water, or 2.1 volumes of hydrogen.

III. 5.1 grams of copper yielded 0.0010 gram of water, or 2.3 volumes of hydrogen.

IV. 5.1 grams of copper yielded 0.0009 gram of water, or 2.1 volumes of hydrogen.

V. 5.1 grams of copper yielded 0.0008 gram of water, or 1.8 volumes of hydrogen.

VI. 5.1 grams of copper yielded 0.0003 gram of water, or 0.7 volume of hydrogen.

The Occlusion of Hydrogen by Silver.

Silver reduced from the oxide takes up minimum amounts of hydrogen, if any.

I. 2.5 grams of silver yielded 0.0001 gram of water, or 0.5 volume of hydrogen.

II. 2.5 grams of silver yielded 0.0005 gram of water, or 2.8 volumes of hydrogen.

III. 5.0 grams of silver yielded 0.0003 gram of water, or 0.8 volume of hydrogen.

This result is in accordance with the results of Graham,[2] whose silver wire occluded 0.2 its volume of the gas, while his metal obtained by reduction of the oxide yielded 0.9 its volume. Neumann and Streintz found no hydrogen in their silver reduced from the oxide.[1]

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[1] Graham: Jsb., 1866, 50; Thudichum and Hake: Jour. Chem. Soc., **33**, (2) 251, (1876); Johnson: Jour. Chem. Soc., **35**, 235; Neumann and Streintz: Monatsh. Chem., **12**, 642; Richards: Proc. Amer. Acad., **26**, 292; and others.

[2] Jsb., 1866, 51.

It is noteworthy that in all the work performed upon the occlusion of hydrogen by the four metals, cobalt, nickel, copper, and silver, when they were reduced from pure oxides at low temperatures, the magnitude of the occlusion varied with the fusion-points of the metals. Cobalt, whose melting-point is the highest, occludes by far the greatest volume of gas; while silver, which melts at the lowest temperature, occludes minimum quantities. The explanation of this peculiarity has already been mentioned. The sintering or fusing together of the metals is greater, the nearer the reduction temperature is to their melting-points; while the surface offered, which determines the amount of occlusion, diminishes with the amount of sintering. Since the melting-points of copper and silver are very near together, one would expect their power of occlusion to be very nearly the same, as is the case.

Pure ferric oxide is not reduced to any considerable extent by hydrogen at the low temperature employed in the case cf the four preceding metals. When a temperature sufficiently high to produce reduction is employed, no appreciable amounts of hydrogen are occluded because of sintering of the metal. On account of this difficulty no work could be done with iron which would be comparable with that done with the other metals.

The question as to the formation of compounds of the metals with hydrogen, similar to "Hydrogenium," is not easily settled. On the one hand, the fact that the quantity of occluded gas varies with the surface presented seems to point to simple condensation on the surface as in the case of charcoal; on the other hand, the pertinacity with which the hydrogen is retained in a vacuum when cold is evidence in the other direction. For the present this point must needs remain undecided.

A word can be profitably said here in regard to the use of the terms "occlusion" and "adsorption." In its stricter sense the word "occlusion" should be confined to an intimate combination, such as that of palladium with hydrogen.

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[1] Monatsh. Chem., **12**, 642.

"Adsorption," on the other hand, refers to simple condensation or concentration in the immediate vicinity of a given surface. Owing to the doubt as to the nature of the process by which the hydrogen is retained by the metals considered, the question as to the designation of the process is necessarily unsettled, but Graham's word has been usually employed above.

In conclusion, I wish to express my thanks to Professor Theodore William Richards for much advice and encouragement given during the course of this work.

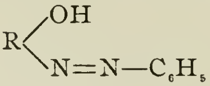
CAMBRIDGE, MASS., June 15, 1899.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE NATURE OF THE OXYAZO COMPOUNDS.

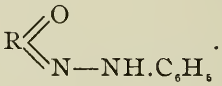
BY WILLIAM MCPHERSON.

The oxyazo compounds have been under investigation for the past fifteen years, especially because no decisive conclusion has been reached as to their constitution. Two general formulæ have been assigned to them; *viz.*,



I.

and



II.

According to the first of these, they are true oxyazo bodies; the second represents them as derivatives of quinones; *viz.*, quinonehydrazones. Goldschmidt, in consequence of results obtained with his students in the case of ortho- and paraoxyazo derivatives decided[1] that these compounds must all be regarded as monohydrazones of quinones or diketones. This conclusion, however, is not in accord with his own previous results obtained with phenyl isocyanate.[2] On the other hand, Jacobson,[3] Meldola,[4] Witt and Schmidt,[5] Noelting and Grandmougin,[6] working chiefly with alkylated substitution-products or in the ortho series, came to conclusions directly opposite to those reached by Goldschmidt.

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[1] Goldschmidt and Brubacher: Ber. d. chem. Ges., **24**, 2300; Goldschmidt and Pollak: *Ibid.*, **25**, 1324.

[2] Goldschmidt and Rosell: *Ibid.*, **23**, 487.

[3] *Ibid.*, **25**, 992; **26**, 681; and **27**, 2700.

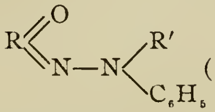
[4] J. Chem. Soc., **53**, 460; **55**, 114 and 603; **59**, 372-710; **63**, 923; **65**, 834.

[5] Ber. d. chem. Ges., **25**, 1013.

[6] *Ibid.*, **24**, 1592.

The oxyazo compounds may conveniently be divided into two classes; namely, those belonging to the ortho series and those belonging to the para series. It does not of necessity follow that the compounds of the one series possess a constitution analogous to that of the other.

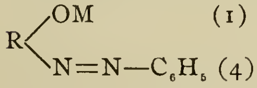
In order to attack this problem from an entirely new standpoint, I undertook, at the suggestion and under the direction of Dr. J. U. Nef, the study of the action of unsymmetrical alkylated and acylated derivatives of phenylhydrazine on various quinones, both of the ortho and the para series. The condensation-products thus obtained,



$$\mathrm{R}\Big<\begin{matrix}\mathrm{O}\\ \mathrm{N-N}\Big<\begin{matrix}\mathrm{R'}\\ \mathrm{C_6H_5}\end{matrix}\end{matrix}$$

(R′= alkyl or acyl),

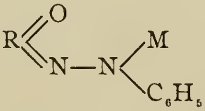
were compared with the free oxyazo compounds and the corresponding products obtained from these by direct alkylation and acylation.[1] The results are decisive; they prove that all paraoxyazo compounds, their salts as well as the acylated and alkylated substitution-products, possess the general formula



$$\mathrm{R}\Big<\begin{matrix}\mathrm{OM} & (1)\\ \mathrm{N{=}N{-}C_6H_5} & (4)\end{matrix}$$

, (M=H, a metal, acyl or alkyl); *i. e.*, all are true oxyazo compounds.

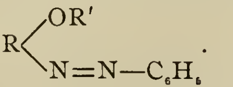
The work in the ortho series, while not so decisive nor so exhaustive, all points now to one conclusion; namely, that these compounds and their acylated substitution-products are monohydrazones of orthodiketones,



$$\mathrm{R}\Big<\begin{matrix}\mathrm{O}\\ \mathrm{N-N}\Big<\begin{matrix}\mathrm{M}\\ \mathrm{C_6H_5}\end{matrix}\end{matrix}$$

(M=H or acyl).

The alkylated substitution-products, on the other hand, are azo compounds,



$$\mathrm{R}\Big<\begin{matrix}\mathrm{OR'}\\ \mathrm{N{=}N{-}C_6H_5}\end{matrix}.$$

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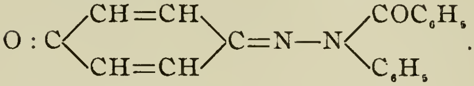
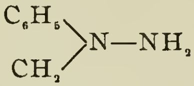
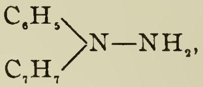
[1] A preliminary notice of my results appeared in the Ber. d. chem. Ges., 28, 2414.

I. THE ACTION OF α-ACYLATED PHENYLHYDRAZINES ON PARAQUINONES.

Quinonebenzoylphenylhydrazone,



$$O:C\left\langle\begin{matrix}CH=CH\\CH=CH\end{matrix}\right\rangle C=N-N\left\langle\begin{matrix}COC_6H_5\\C_6H_5\end{matrix}\right. .$$

Benzoquinone and its homologues react with phenylhydrazine with evolution of nitrogen and formation of resinous products.[1] Since hydroxylamine[2] and its α-alkylated substitution-products[3] react in a normal manner with quinone, it seemed possible that a replacement of the imide hydrogen in phenylhydrazine by acyl or alkyl might give rise to products which would condense in a normal manner with paraquinones; whereas, it was found that α-methyl and α-benzylphenylhydrazine,  $\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\rangle N-NH_2$ and  $\left.\begin{matrix}C_6H_5\\C_7H_7\end{matrix}\right\rangle N-NH_2$, react with benzo-, toluo-, and thymoquinone with formation of hydroquinone and tetrazones (see below); α-naphthoquinone reacts, just as with phenylhydrazine itself in a perfectly normal manner with these reagents. All these quinones, however, give normal condensation-products on treatment with α-acylated phenylhydrazines.

One and two-tenths grams of α-benzoylphenylhydrazine hydrochloride, made according to the directions of Widman,[4] were dissolved in 300 cc. of water containing a few drops of hydrochloric acid. To this was added a solution of 0.5 gram benzoquinone in 200 cc. of water. A yellow precipitate begins to separate out at once and, after two hours, the reaction is completed. Yield 1.3 grams (theory 1.4 grams). The substance was purified by recrystallizing twice from benzene, in which it readily dissolves while hot and from which it is deposited on cooling in yellow, flat needles or in prisms melting at 171°.

0.1870 gram substance gave 15.5 cc. nitrogen at 24.5° and 744.8 mm.

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[1] Zincke: Ber. d. chem. Ges., **16**, 1563.

[2] Goldschmidt: *Ibid.*, **17**, 213.

[3] Bridge: Ann. Chem. (Liebig), **277**, 90, 95.

[4] Ber. d. chem. Ges., **26**, 945.

0.1961 gram substance gave 0.5410 gram CO_2, and 0.0900 gram H_2O.

	Calculated for $C_{19}H_{14}N_2O_2$.	Found.
C	75.49	75.22
H	4.63	5.10
N	9.29	9.15

Quinonebenzoylphenylhydrazone is very difficultly soluble in cold ether and alcohol. It separates out from hot alcohol in groups of crystals resembling sodium chloride ; if the solution, however, is cooled very slowly, heavy, transparent, reddish-yellow crystals with numerous well-defined facets are obtained. The substance is readily soluble in chloroform and glacial acetic acid, moderately soluble in cold benzene, and insoluble in ligroin, and can therefore also be purified by crystallizing from a mixture of benzene and ligroin.

Behavior towards Reducing Agents.

Quinonebenzoylphenylhydrazone (1 gram) treated in cold acetic acid solution with zinc dust is split, in a few minutes, quantitatively into benzanilide and paramidophenol ; on addition of water to the filtered solution, benzanilide separates out in plates (0.55 gram). These were purified by distillation and subsequent crystallization from alcohol. Yield, 0.3 gram of pure product melting at 161°.

0.2454 gram substance gave 16.1 cc. nitrogen at 26°.2 and 743.8 mm.

	Calculated for $C_{13}H_{11}NO$.	Found.
N	7.11	7.15

The presence of paramidophenol in the filtrate was established, after precipitating the zinc with hydrogen sulphide, by converting it into the hydrochloride and then by means of calcium hypochlorite[1] into quinonechlorimide ; melting-point found, 85°.

This decomposition, which was also established in the case of the corresponding derivatives of toluo-, thymo-, and α-naphthoquinone, is entirely analogous to those observed by Goldschmidt[2] in the reduction of a whole series of acetyl and benzoyl derivatives of orthooxyazo compounds both in the benzene as well as in the naphthalene series. This proves that the conclusions drawn by him from those results, *viz.*, that the acyl groups are bound to nitrogen and not to oxygen are entirely justifiable.

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[1] Fogh : Ber. d. chem. Ges., **21**, 890.

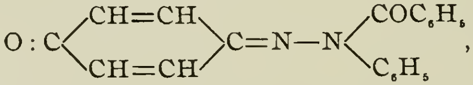
[2] *Ibid.*, **24**, 2300, and **25**, 1324.

Behavior towards Phenylhydrazine.

Quinonebenzoylhydrazone reacts on addition of phenylhydrazine with such explosive violence that complete charring takes place. Even in dilute alcoholic or acetic acid solutions, decolorization, with decided evolution of heat and of nitrogen, takes place. This substance therefore behaves towards this reagent in a manner analogous to quinone and its homologues.

Comparison with Goldschmidt's so-called Quinonebenzoylphenylhydrazone.

The quinonebenzoylphenylhydrazone described above, which, from its method of synthesis and its properties, unquestionably possesses the constitution,



$$O:C\left\langle\begin{matrix}CH=CH\\CH=CH\end{matrix}\right\rangle C=N-N\left\langle\begin{matrix}COC_6H_5\\C_6H_5\end{matrix}\right.,$$

is *isomeric*, *not identical*, with the benzoyl derivative which can be obtained from paraoxyazobenzene by means of Baumann's reaction, or directly by heating it with benzoic anhydride. The benzoate of paraoxyazobenzene melts at 138° and crystallizes from alcohol, as was observed in a preparation made according to Tschirwinsky's directions,[1] in thin, voluminous, yellow plates or scales. Zinc and acetic acid convert it into the colorless dihydride described by Goldschmidt and Brubacher[2] (melting-point found, 172°.5). This compound is readily converted, as I have observed, by adding ferric chloride or mercuric oxide to its alcoholic solution, back again into the yellow benzoate of paraoxyazobenzene. Tschirwinsky's benzoate of paraoxyazobenzene is furthermore split in the cold by treatment with concentrated sulphuric acid or with alcoholic potash into benzoic acid and paraoxyazobenzene. This compound must therefore possess the constitution,

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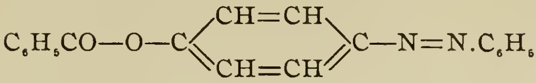
[1] Ber. d. chem. Ges., **6**, 561.

[2] *Ibid.*, **24**, 2302; and **25**, 1325.



$$C_6H_5CO{-}O{-}C\left\langle\begin{matrix}CH{=}CH\\ CH{=}CH\end{matrix}\right\rangle C{-}N{=}N.C_6H_5,$$

and not the isomeric formula given it by Goldschmidt and Brubacher; its dihydride, discovered by Goldschmidt and Brubacher, is therefore the corresponding hydrazo derivative,

$$C_6H_5CO{-}O{-}C_6H_4{-}NH{-}NH{-}C_6H_5.$$

Goldschmidt has indeed given all the acetyl and benzoyl derivatives of paraoxyazo compounds the quinonehydrazone formula, *i. e.*, he assumes that the acyl group introduced is bound to nitrogen and not to oxygen. He was never able, however, to bring forward decisive experimental proof for this assumption in the case of paraoxyazo compounds. He never succeeded, for example in establishing a splitting of these compounds into acetanilide or benzanilide, respectively, as he had done in the case of the orthooxyazo compounds. His conclusions were therefore based chiefly on the conviction that all oxyazo compounds, the ortho as well as the para, must possess an analogous constitution, a conclusion which, as is now evident, was not justifiable.

A comparison of the quinone derivatives obtained by means of α-benzoylphenylhydrazine, from toluo-, thymo-, and α-naphthoquinone, with the corresponding benzoates from benzeneazoorthocresol, benzeneazothymol, benzeneazo-α-naphthol, in like manner establishes that the products are isomeric and not identical (see below).

Behavior of Quinonebenzoylphenylhydrazone towards Saponifying Agents.

The behavior of the actual quinonebenzoylphenylhydrazone towards concentrated sulphuric acid and alcoholic potash is very interesting. It is split, after standing in the cold, quantitatively into benzoic acid and paraoxyazobenzene. The same result is obtained on adding dilute hydrochloric acid to a hot alcoholic solution of the substance. The experiment was carried out in every case with 0.5 gram of material and the paraoxyazobenzene obtained very carefully compared with a preparation made in the ordinary manner. All products melted at 152° and crystallized from benzene in peculiar flat crystals grouped together. Furthermore, they were all converted by means of Baumann's reaction into the ordinary benzoylated paraoxyazobenzene,

$$C_6H_5CO—O—C_6H_4N=NC_6H_5,$$

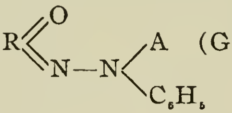
of Tschirwinsky (melting-point observed, 138°, thin plates).

These experiments prove that, on saponification, quinonebenzoylphenylhydrazone, as well as its isomer, the benzoate of paraoxyazobenzene, give one and the same product; *viz.*, paraoxyazobenzene, $OH—C_6H_4N_2—C_6H_5$. That this substance possesses a constitution represented by its name, that it is not quinonephenylhydrazone,

$$O=C_6H_4=N—NH—C_6H_5,$$

or a tautomeric compound, the following facts establish beyond a reasonable doubt:

1. Paraoxyazobenzene, by direct acylation of alkylation, gives acyl as well as alkyl derivatives, which unquestionably and exclusively contain the acyl as well as the alkyl group bound to oxygen, $C_6H_5—N_2—C_6H_4—OM$ (M=acyl or alkyl). This is proved in the case of the acyl derivatives by the experiments described in this paper, and in the case of the alkyl derivatives by the experiments of Jacobson.[1]

2. The orthooxyazo derivatives by direct acylation give products which as unquestionably contain the acyl group bound exclusively to nitrogen,  $R\left\langle\begin{array}{l}O\\ N—N\left\langle\begin{array}{l}A\\ C_6H_5\end{array}\right.\end{array}\right.$ (Goldschmidt and others).

3. The free paraoxyazo compounds do not react, as I have observed, in the case of paraoxyazobenzene and others, with phenylhydrazine, either directly or in alcoholic solution, even if heated to 100°, whereas all paraquinonebenzoylphenylhydrazone derivatives, like benzoquinone itself, react with this reagent with explosive violence. Were oxyazobenzene identical with quinonehydrazone, $O:C_6H_4=N—NH—C_6H_5$, it is

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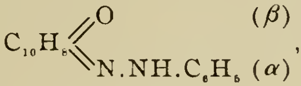
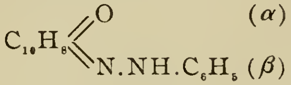
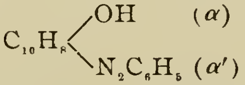
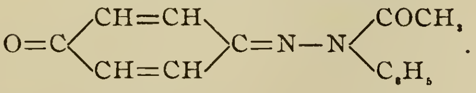
[1] *Loc. cit.*

difficult to understand its indifference to phenylhydrazine as compared with the intense activity of its nitrogen-acylated derivatives.

4. The paraoxyazo compounds are all freely soluble in dilute caustic alkalies and in some cases even in dilute alkaline carbonates; in marked contrast is the behavior of the orthooxyazo compounds of the naphthalene series which are unquestionably quinonehydrazones. Thus benzeneazo-β-naphthol,  $C_{10}H_6\left\langle\begin{array}{ll}O & (\beta)\\ N.NH.C_6H_5 & (\alpha)\end{array}\right.$, and β-naphthoquinone-phenylhydrazone,  $C_{10}H_6\left\langle\begin{array}{ll}O & (\alpha)\\ N.NH.C_6H_5 & (\beta)\end{array}\right.$, are insoluble in and not affected by most concentrated caustic alkalies.[1] The isomeric para compound,  $C_{10}H_6\left\langle\begin{array}{ll}OH & (\alpha)\\ N_2C_6H_5 & (\alpha')\end{array}\right.$, which remarkably enough is formed when α-naphthoquinone is treated with phenylhydrazine,[2] is, on the other hand, easily soluble even in alkaline carbonates. These noteworthy differences become self-evident if the paraoxyazo compounds are regarded as phenols.

5. A study of the physical properties of the free paraoxyazo compounds, carried out after my preliminary experiments, has led Auwers and Orton[3] to results entirely in accord with those obtained by chemical methods.

Quinoneacetylphenylhydrazone,



$$O{=}C\left\langle\begin{array}{l}CH{=}CH\\ CH{=}CH\end{array}\right\rangle C{=}N{-}N\left\langle\begin{array}{l}COCH_3\\ C_6H_5\end{array}\right. .$$

The α-acetylphenylhydrazine used to prepare this compound was made from acetylformazylhydride according to Peckmann's directions[4] and also by Widman's method.[5] The latter method is more convenient. 0.5 gram of α-acetylphenylhydrazine hydrochloride was dissolved in 25 cc. of water and acidified with a few drops of hydrochloric acid ; to this was added a solution of 0.4 gram benzoquinone in 30 cc. of 10 per cent alcohol. Yellow crystals soon began to separate out ; after half an hour these were filtered off and dried (yield, 0.58 gram). Recrystallized from a mixture of benzene and ligroin, the substance was obtained in flat, yellow needles melting at 118°.

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[1] Liebermann: Ber. d. chem. Ges., **16**, 2858; Zincke and Bindewald: *Ibid.*, **17**, 3031.

[2] Zincke and Bindewald: *Ibid.*, **17**, 3026.

[3] Zeit. phys. Chem., **21**, 356.

[4] V. Peckmann: Ber. d. chem. Ges., **27**, 1695.

[5] Widman: *Ibid.*, **27**, 2964.

0.2238 gram substance gave 24.2 cc. nitrogen at 25° and 743.3 mm.

0.1794 gram substance gave 0.4587 gram CO_2, and 0.0800 gram H_2O.

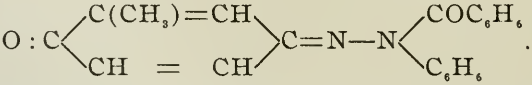
	Calculated for $C_{14}H_{12}N_2O_2$.	Found.
C	70.00	69.73
H	5.00	4.95
N	11.66	11.86

The substance is very soluble in benzene and chloroform, less so in alcohol and ether. It reacts violently with phenylhydrazine and is converted by alcoholic potash or concentrated sulphuric acid into paraoxyazobenzene. It is *isomeric, not identical*, with the acetate or paraoxyazobenzene,

$$C_6H_5N_2—C_6H_4—O—CO—CH_3,$$

which has been prepared by Wallach and Kiepenhauer ;[1] the latter substance, prepared according to their directions, was found to crystallize from benzene-ligroin in plates melting at 89°.5, instead of 84°–85°, as given by these observers. Alcoholic potash splits it into paraoxyazobenzene and acetic acid.

Toluquinonebenzoylphenylhydrazone,



$$\mathrm{O:C}\left\langle\begin{array}{l}\mathrm{C(CH_3)=CH}\\ \mathrm{CH\ =\ CH}\end{array}\right\rangle\mathrm{C{=}N{-}N}\left\langle\begin{array}{l}\mathrm{COC_6H_6}\\ \mathrm{C_6H_6}\end{array}\right. .$$

Toluquinone, 0.4 gram, dissolved in 120 cc. of dilute alcohol, was added to a solution of 1 gram α-benzoylphenylhydrazine sulphate in 180 cc. of 10 per cent alcohol. A yellow precipitate began to separate out at once. After two hours this was filtered off and recrystallized three times from benzene.

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[1] Wallach and Kiepenhauer : Ber d. chem. Ges., 14, 2617.

0.1892 gram substance gave 0.5181 gram CO_2, and 0.0921 gram H_2O.

0.1732 gram substance gave 13.9 cc. nitrogen at 23°.5 and 745 mm.

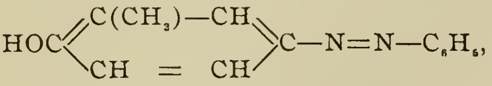
	Calculated for $C_{20}H_{16}N_2O_2$.	Found.
C	75.94	75.89
H	5.06	5.50
N	8.86	8.90

Toluquinonebenzoylphenylhydrazone is very soluble in ether and chloroform, moderately so in benzene, alcohol, and acetone. It separates from benzene or from benzene-ligroin in small, square, yellow tablets, melting at 151°. From alcohol it is deposited in red tablets or in yellow, feathery crystals. Treated with zinc dust and acetic acid, the hydrazone (0.5 gram) is split into benzanilide, melting-point 151°. A nitrogen determination gave the following result:

0.2132 gram substance gave 14.3 cc. nitrogen at 22° and 746 mm.

	Calculated for $C_{13}H_{11}NO$.	Found.
N	7.11	7.59

That the hydrazone has the constitution above given is proved by its method of synthesis and by its conversion, on treatment with alcoholic potash, into benzeneazoorthocresol,

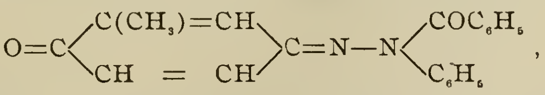


$$\mathrm{HOC}\left\langle\begin{array}{l}\mathrm{C(CH_3)-CH}\\ \mathrm{CH\ =\ CH}\end{array}\right\rangle\mathrm{C-N=N-C_6H_5},$$

obtained in yellow plates melting at 128°–130°.

Comparison with Goldschmidt's So-called Toluquinonebenzoylphenylhydrazone.

The compound described above, which from its method of synthesis and reactions must possess the constitution,



$$\mathrm{O=C}\left\langle\begin{array}{l}\mathrm{C(CH_3)=CH}\\ \mathrm{CH\ =\ CH}\end{array}\right\rangle\mathrm{C=N-N}\left\langle\begin{array}{l}\mathrm{COC_6H_5}\\ \mathrm{C_6H_5}\end{array}\right.,$$

is *isomeric*, *not identical*, with the benzoate of benzeneazoorthocresol, first described by Noelting and Kohn,[1] and afterwards,

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[1] Liebermann and Kostanecki: Ber. d. chem. Ges., **17**, 131, 879: Cf. Noelting and Kohn: *Ibid.*, **17**, 366.

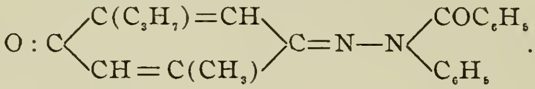
(as well as the corresponding acetate), regarded by Goldschmidt[1] as being a quinone derivative. The latter compound melts at 110°, and is split by alcoholic potash into benzeneazoorthocresol. Its dihydride melts at 142°, and is readily oxidized to the original benzoyl derivative by means of ferric chloride. It is evident therefore that the formula given by Goldschmidt to the acylated derivatives of benzeneazoorthocresol and their dihydrides must be changed to

$$AO—C_6H_3(CH_3)—N=N—C_6H_5$$

and $$AO—C_6H_3(CH_3)—NH—NH—C_6H_5,$$

respectively.

Thymoquinonebenzoylphenylhydrazone,



$$O:C\left\langle\begin{matrix}C(C_3H_7)=CH\\ CH=C(CH_3)\end{matrix}\right\rangle C=N—N\left\langle\begin{matrix}COC_6H_5\\ C_6H_5\end{matrix}\right..$$

Four grams α-benzoylphenylhydrazine sulphate, dissolved in 350 cc. of 14 per cent alcohol, were added to a solution of 2 grams of thymoquinone in 300 cc. of 33 per cent alcohol. The mixture was heated until the quinone, partially precipitated, had redissolved and then allowed to stand twenty-four hours, when the yellow precipitate was filtered off. On examination this was found to be a mixture of two products, one yellow, the other colorless.[2] Their separation was accom-

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[1] Ber. d. chem. Ges., **25**, 1331.

[2] In the interaction between acylated hydrazines and quinones, it was generally found best to add a concentrated alcoholic solution of the quinone to an aqueous solution of the hydrazine salt whereby the quinone is at first precipitated in a finely divided condition. It was found, however, that if the reaction in the above instance was carried out in this way, the principal product was a crystalline substance, which is best purified by washing with small quantities of cold benzene, and then dissolving the insoluble part in hot benzene with addition of animal charcoal. On filtering and cooling, snow-white needles melting at 155° were obtained.

0.2030 gram substance gave 21 cc. nitrogen at 20°.5 and 736.4 mm.

0.1749 gram substance gave 17.7 cc. nitrogen at 19° and 736 mm.

0.1705 gram substance gave 0.4437 gram CO_2, and 0.0853 gram H_2O.

0.1730 gram substance gave 0 4512 gram CO_2, and 0.0868 gram H_2O.

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.	
C	70.86	70.96	71.12
H	5.51	5.56	5.56
N	11.02	11.40	11.31

Small amounts of a colorless substance were also obtained in the case of toluo- and of α-naphthoquinone. Inasmuch as these seemed to have no particular bearing on the subject under investigation, no further study of them has yet been made, although it is my intention to examine them later.

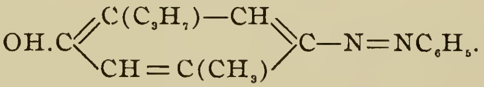
plished by repeated treatment with small amounts of cold benzene which dissolves only the yellow product; recrystallized from benzene-ligroin, the last-named substance was obtained in yellow plates melting at 132°.

0.1746 gram substance gave 13 cc. nitrogen at 23° and 745 mm.

0.1739 gram substance gave 0.4892 gram CO_2, and 0.1003 gram H_2O.

	Calculated for $C_{23}H_{22}N_2O_2$.	Found.
C	77.09	76.71
H	6.14	6.41
N	7.82	8.20

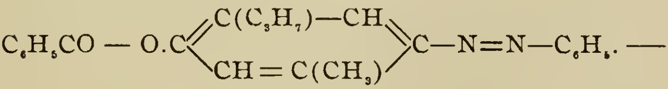
Thymoquinonebenzoylhydrazone is very soluble in chloroform and benzene, moderately so in alcohol, and with difficulty in ether. Reduced with zinc dust and acetic acid in the cold, it is split into benzanilide, melting-point 163°. Saponified by means of alcoholic potash, it gives benzoic acid and benzeneazothymol,[1] melting-point 93°.



$$\mathrm{OH.C}\left\langle\begin{matrix}\mathrm{C(C_3H_7)-CH}\\ \mathrm{CH=C(CH_3)}\end{matrix}\right\rangle\mathrm{C-N=NC_6H_5.}$$

This, together with the method of synthesis, proves the constitution of the quinonehydrazone to be that given above.

Benzoate of Benzeneazothymol,



$$\mathrm{C_6H_5CO-O.C}\left\langle\begin{matrix}\mathrm{C(C_3H_7)-CH}\\ \mathrm{CH=C(CH_3)}\end{matrix}\right\rangle\mathrm{C-N=N-C_6H_5.}$$

— This substance was prepared from benzeneazothymol by means of Baumann's reaction, in order to compare it with the isomeric quinone derivative just described. Recrystallized twice from hot alcohol, it was obtained in reddish-yellow needles melting at 115°. It is consequently *isomeric*, and *not identical*, with the product in question.

0.2195 gram substance gave 16.2 cc. nitrogen at 22° and 740 mm.

0.2081 gram substance gave 0.5881 gram CO_2, and 0.1151 gram H_2O.

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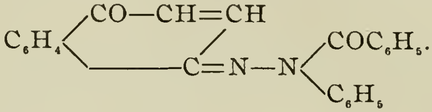
[1] Mazzari and Passetto: Gazz. chim. ital., **15**, 53.

	Calculated for $C_{23}H_{22}N_2O_2$.	Found.
C	77.09	77.05
H	6.14	6.15
N	7.82	8.18

The benzoate of benzeneazothymol is very soluble in hot benzene and chloroform, moderately so in ether and ligroin. It is converted by means of alcoholic potash into benzoic acid and benzeneazothymol, whose melting-point was found to be 93° and not 85°–90°, as given by Mazzari and Possetto.

α-Naphthoquinonebenzoylphenylhydrazone,



Two grams of α-naphthoquinone, dissolved in a small amount of alcohol, were poured into a liter of water, and thereupon an excess (5 grams) of α-benzoylphenylhydrazine sulphate, dissolved in 200 cc. of 40 per cent alcohol, added. The mixture was heated to 70°–80° and then allowed to stand for twenty-four hours. The crude product, 4.5 grams, was purified by repeated crystallization from benzene-ligroin, and obtained in yellow silky needles, melting at 161°.5.

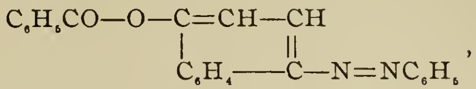
0.1848 gram substance gave 0.5312 gram CO_2, and 0.0814 gram H_2O.

0.2641 gram substance gave 18.7 cc. nitrogen at 25° and 745.3 mm.

	Calculated for $C_{23}H_{16}N_2O_2$.	Found.
C	78.40	78.35
H	4.54	4.90
N	7.95	7.78

The substance is very soluble in benzene; it dissolves less readily in ether and alcohol, and is insoluble in ligroin. Reduced with zinc dust and acetic acid, it is split into benzanilide. Alcoholic potash converts it into benzeneazo-α-naphthol, melting-point 205°, from which was obtained the benzoate, melting-point 121°.5.

The benzoate of benzeneazo-α-naphthol,

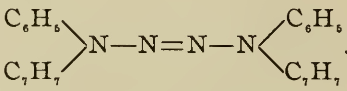


$$\begin{array}{l} C_6H_5CO{-}O{-}C{=}CH{-}CH \\ \qquad\qquad\quad | \qquad\quad \| \\ \qquad\qquad C_6H_4{-\!-\!-}C{-}N{=}NC_6H_5 \end{array},$$

has been prepared by Meldola;[1] it is *isomeric*, *not identical*, with the compound just described, and consequently must have its benzoyl group bound to oxygen. The formulæ given by Goldschmidt and Brubacher[2] to the acylated derivatives of α-naphthoquinonehydrazone or benzeneazo-α-naphthol and the corresponding dihydrides are therefore incorrect. The benzoate derivative can easily be prepared by Baumann's reaction, using barium hydroxide instead of sodium hydroxide. It is very slightly soluble in alcohol, ether, and hot ligroin, and always separates out in yellow needles melting at 121°.5. The two modifications described by Meldola were never observed.

II. ACTION OF α-ALKYLATED PHENYLHYDRAZINES ON PARA-QUINONES.

Diphenyldibenzyltetrazone,



$$\begin{matrix}C_6H_5\\C_7H_7\end{matrix}{>}N{-}N{=}N{-}N{<}\begin{matrix}C_6H_5\\C_7H_7\end{matrix}.$$

—When benzoquinone and α-methylphenylhydrazine hydrochloride are brought together in dilute aqueous solution, an evolution of nitrogen is observed, and dimethyldiphenyltetrazone (melting-point 133°) separates out in leaflets (50 per cent of the calculated quantity).

Equimolecular proportions of benzoquinone and α-benzylphenylhydrazine sulphate (made by Widman's method) react at once in dilute aqueous solution; a strong odor of benzaldehyde is noticed and a bright yellow precipitate appears. After three hours' standing this was filtered off and purified by treatment in benzene solution with animal charcoal and repeated crystallization from benzene-ligroin. Colorless rhombohedra, melting with decomposition at 145°, were obtained. Philips[3] mentions a substance melting at 109°, obtained by him from benzylphenylhydrazine by oxidation with mercuric oxide; no analysis is given and it is evident that the product was very impure.

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[1] J. Chem. Soc., **55**, 606.

[2] Ber. d. chem. Ges., **24**, 2313-14.

[3] *Ibid.*, **20**, 2487.

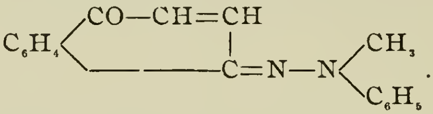
0.2040 gram substance gave 26.7 cc. nitrogen at 23° and 749.3 mm.

0.1648 gram substance gave 0.4822 gram CO_2, and 0.0895 gram H_2O.

	Calculated for $C_{26}H_{24}N_4$.	Found.
C	79.59	79.79
H	6.12	6.03
N	14.29	14.61

The action of α-alkylated phenylhydrazines on tolu- and thymoquinone is similar to that described in the case of benzoquinone.

α-Naphthoquinonemethylphenylhydrazone,



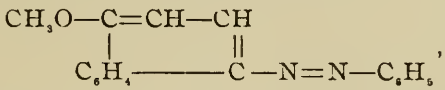
A solution of 5 grams of α-naphthoquinone in a small amount of alcohol was poured into a liter of water. To this was added a solution of 6 grams of α-methylphenylhydrazine sulphate in 200 cc. of 10 per cent alcohol. A slight evolution of gas was observed, and, after standing over night, a dark-red, very bulky precipitate appeared. The crude product, 6.2 grams, was purified by crystallizing three times from benzene-ligroin, and thus obtained in long, flat, amethyst-colored crystals which assume a metallic luster when powdered, and melt at 118°.5.

0.2398 gram substance gave 22.5 cc. nitrogen at 24° and 745 mm.

0.1550 gram substance gave 0.4404 gram CO_2, and 0.0765 gram H_2O.

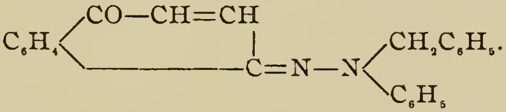
	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.48
H	5.34	5.48
N	10.68	10.40

The quinonehydrazone is very soluble in benzene and chloroform, moderately so in alcohol and ether, and insoluble in cold ligroin. The substance is *isomeric, not identical*, with the methyl ether obtained from benzeneazo-α-naphthol;[1] this compound, made according to the directions of Zincke and Bindewald, was separated from resinous products by means of cold ligroin, brown needles melting at 82°–83°. The latter compound must therefore possess the formula,



as has already been made probable by the experiments of Witt and Schmidt,[2] and others.

α-Naphthoquinonebenzylphenylhydrazone,



α-Naphthoquinone, 0.5 gram, dissolved in a small amount of alcohol, was poured into 300 cc. of water, and then a solution of 1 gram of α-benzylphenylhydrazine sulphate in 50 cc. of 10 per cent alcohol, which had been acidified with 2 cc. of strong sulphuric acid, was added. After standing over night, a tarry, dichroic mass had separated out which readily solidified when scratched. The product was obtained pure only after eight crystallizations from benzene-ligroin. It is very soluble in chloroform and benzene, sparingly soluble in alcohol and ether, and was obtained from benzene-ligroin in yellow, dichroic, flat needles, melting at 136°.

0.1998 gram substance gave 15.5 cc. nitrogen at 24° and 741.5 mm.

0.1876 gram substance gave 0.5632 gram CO_2, and 0.0962 gram H_2O.

	Calculated for $C_{23}H_{18}N_2O$.	Found.
C	81.65	81.80
H	5.30	5.55
N	8.26	8.52

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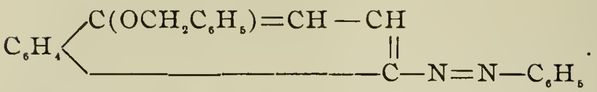
[1] Zincke and Bindewald: Ber. d. chem. Ges., **17**, 3026.

[2] *Ibid.*, **25**, 1013

Benzyl Ether of Benzeneazo-α-naphthol,



An alcoholic solution of 5 grams benzeneazo-α-naphthol, prepared from α-naphthol and phenyldiazonium nitrate, was treated with 1.6 grams caustic soda and 5 grams benzyl chloride. The reaction was complete after five hours' heating. The product obtained was separated from some tar by recrystallizing from benzene-ligroin. It is very soluble in benzene but insoluble in ligroin. It consists of ruby-red, monoclinic crystals, which melt at 102°. When powdered, these become yellow.

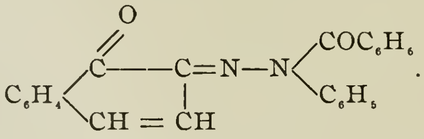
0.1962 gram substance gave 15.4 cc. nitrogen at 28°.5 and 748.8 mm.

0.2000 gram substance gave 0.6020 gram CO_2, and 0.1020 gram H_2O.

	Calculated for $C_{23}H_{18}N_2O$.	Found.
C	81.65	82.08
H	5.30	5.66
N	8.26	8.51

III. THE ACTION OF α-ALKYLATED AND OF α-ACYLATED PHENYLHYDRAZINES ON β-NAPHTHOQUINONEHYDRAZONE.

The Benzoate of β-Naphthoquinonephenylhydrazone is Identical with β-Naphthoquinonebenzoylphenylhydrazone,



The benzoyl derivative of β-naphthoquinonehydrazone can readily be prepared by adding benzoyl chloride to an alcoholic solution of the hydrazone, containing 1 molecule of sodium ethylate. Reaction takes place in the cold. The benzoate formed was purified by recrystallization from benzene-ligroin. It forms yellow needles, melting at 191°, sparingly soluble even in hot alcohol, and fairly soluble in benzene.

0.2524 gram substance gave 18.6 cc. nitrogen at 24°.5 and 740.3 mm.

0.2080 gram substance gave 0.5983 gram CO_2, and 0.0904 gram H_2O.

	Calculated for $C_{23}H_{16}N_2O_2$.	Found.
C	78.40	78.44
H	4.54	4.83
N	7.95	8.07

The substance is readily split into its components, benzoic acid and β-naphthoquinonehydrazone, melting-point 138°, by treatment either with alcoholic potash or with concentrated sulphuric acid.

It can also be prepared from the hydrazone by heating with benzoic anhydride to 150° for five hours.

The corresponding acetate of β-naphthoquinonehydrazone has been prepared by Meldola[1] by means of acetic anhydride. This compound gives, according to Meldola, acetanilide on reduction with zinc dust and acetic acid. It can be obtained quantitatively, as I have found, by heating 5 grams of the hydrazone with 50 grams acetic anhydride and 20 grams fused sodium acetate for six hours at 100°.

That the benzoate of β-naphthoquinonehydrazone has the benzoyl group bound to nitrogen, is proved by its synthesis from β-naphthoquinone and α-benzoylphenylhydrazine sulphate. When these reagents are brought together in a dilute alcoholic solution, in a manner analogous to other cases described in this paper, a reaction takes place at once, even at 0°, with separation of a yellow precipitate. This product is so unstable that all attempts to purify it failed ; after filtration it is rapidly converted into a tarry mass. If the reaction is effected at higher temperatures, however, a normal condensation results. Two grams of the sulphate were dissolved in 180 cc. of 20 per cent. alcohol, and heated to boiling. As soon as the air is expelled from the flask, a solution of 1 gram of β-naphthoquinone in 50 cc. of alcohol, was slowly added, and the boiling continued for twenty minutes. A bright-yellow precipitate separates out which gradually becomes tarry; on decanting and washing with hot alcohol, the impurities dissolve and leave a yellow crystalline residue, which, after recrystallization from benzene-ligroin, was obtained in yellow needles, melting at 191°, and identical in all their properties with the benzoate of β-naphthoquinonehydrazone just described.

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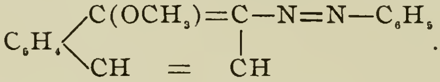
[1] J. Chem. Soc., **65**, 839.

Methyl Ether of β-Benzeneazo-α-naphthol,



$$C_6H_4\left\langle\begin{array}{l} C(OCH_3)=C-N=N-C_6H_5 \\ \qquad\qquad\quad\;\; | \\ CH \quad = \quad CH \end{array}\right. .$$

The experiments of Meldola and of Noelting and Grandmougin[1] with β-naphthoquinonehydrazone, have already made it highly probable that the ethers obtained from this compound, by means of alkalies and alkyl haloids, contain the alkyl group bound to oxygen. The following experiments confirm these conclusions.

Two grams β-naphthoquinonehydrazone and 3 grams of methyl iodide were added to an alcoholic solution containing sodium methylate (from 0.5 gram sodium), and the mixture was heated to boiling for five hours. The methyl ether was precipitated by adding water and recrystallized several times from alcohol. It forms reddish-yellow plates readily soluble in benzene and hot alcohol, melting at 95°.

0.2234 gram substance gave 21.4 cc. nitrogen at 23° and 740 mm.

0.1622 gram substance gave 0.4609 gram CO_2, and 0.0753 gram H_2O.

	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.49
H	5.34	5.15
N	10.68	10.47

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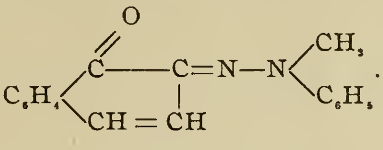
[1] Meldola: J. Chem. Soc., 65, 834; Cf. also Noelting and Grandmougin: Ber. d. chem. Ges., 24, 1592.

β-Naphthoquinonemethylphenylhydrazone,



Four grams of α-methylphenylhydrazine sulphate were dissolved in 500 cc. of water, containing 50 cc. of glacial acetic acid, and the mixture heated to 70°–80°. Thereto were slowly added 3 grams of β-naphthoquinone, dissolved in a small amount of alcohol, and the temperature kept at 80° for two hours. On cooling, the condensation-product was filtered off and recrystallized, after treatment with animal charcoal, from benzene-ligroin. It formed yellow nodules, melting at 134.5°, very soluble in benzene, and sparingly soluble in hot alcohol, from which, on cooling, needle-shaped crystals are obtained. The yield is small, not more than 2 per cent.

0.1834 gram substance gave 17.2 cc. nitrogen at 22° and 742 mm.

0.1632 gram substance gave 0.4644 gram CO_2, and 0.0797 gram H_2O.

	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.60
H	5.34	5.42
N	10.68	10.41

From the facts presented in this paper, and from previous experiments by Goldschmidt, Meldola, and others, it follows that β-naphthoquinonehydrazone is a quinone derivative; it gives by direct acylation, or by treatment with benzoyl chloride and sodium ethylate, acylated derivatives in which the acyl group is unquestionably and exclusively bound to nitrogen. With alkyl iodides and alkalies, on the other hand, it is converted into alkyl ethers, in which the alkyl group is undoubtedly and exclusively bound to oxygen. It is highly probable from facts recorded in the literature that all ortho-oxyazo compounds show a similar deportment on acylation and alkylation.

A CONTRIBUTION TO THE STUDY OF LIQUID MIXTURES OF CONSTANT BOILING-POINT.[1]

BY GARNETT RYLAND.

INTRODUCTION.

In the course of an investigation undertaken for another purpose a mixture of methyl alcohol and benzene was subjected to a fractional distillation, when it was observed that the larger part boiled like a homogeneous liquid at 57°–58°, and could not be separated by repeated distillation with a Hempel tube. By making trial mixtures it was found that, mixed in certain definite proportions, methyl alcohol and benzene will boil to the last drop at 57°–57°.5, under atmospheric pressure. If there is present an excess of either of the constituents, the constant boiling mixture and this excess are separated by fractional distillation. As roughly determined, the proper ratio seemed approximately $3CH_4O : 2C_6H_6$ (38.1 parts of alcohol to 61.9 parts of benzene, by weight).

On examination of the literature no such observation of this mixture could be found, though several similar phenomena are on record.

Historical Sketch.

1. H. E. Roscoe[2] investigated certain aqueous acids of constant boiling-point, which had been regarded as definite hydrates, and found that the proportions of water and acid were not those required by any simple molecular ratio, nor did the composition remain the same when the pressure varied.

Aqueous nitric acid, when distilled under a pressure of 735 mm., always gave a residue which boiled at 120°.5, and contained 68 per cent of pure acid. Distilled under 75 mm.

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[1] From the dissertation submitted by the author to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1898. The investigation was undertaken at the suggestion of Professor Remsen, and carried on under his supervision.

[2] "On the Composition of Aqueous Acids of Constant Boiling-point." J. Chem. Soc., **13**, 146 (1861), and **15**, 270 (1862).

pressure, the per cent of pure acid was 66.7; and under 1260 mm. it became 68.8.

Aqueous solutions of hydrochloric, hydrobromic, and hydriodic acid gave similar phenomena, only in these cases the per cent of acid increased as temperature and pressure decreased. Hydrofluoric acid resembled nitric acid in all respects.

Aqueous formic acid containing 77.5 per cent of pure acid (boiling-point 101°.1), boiled at the fixed temperature of 107°.1, under 760 mm. pressure, the proportion of acid increasing with the pressure.

Aqueous perchloric acid[1] gave a residue which boiled constantly at 203°, under atmospheric pressure, and contained 71.6 per cent pure acid.

2. Alexander Bauer[2] found that a mixture of ethylene bromide (boiling-point 129°) and propylene bromide (boiling-point 141°) in equivalent amounts, distilled at 134°, and could not be separated by fractionation.

3. J. A. Wanklyn[3] called attention to the fact that in the distillation of a mixture of liquids the proportions in which the constituents pass over depend not merely on their relative quantity and on their respective vapor-tensions at the temperature of ebullition, but also upon their mutual adhesion and on the density of their vapors.

On distilling a mixture of 18 grams of methyl alcohol (boiling-point 66°) and 17 grams of ethyl iodide (boiling-point 72°), the first third of the distillate contained a greater amount of the less volatile than of the more volatile liquid.

4. Berthelot[4] stated that a mixture of 91 parts carbon disulphide (boiling-point 48°) and 9 parts alcohol (boiling-point 78°), by weight, boils at 43°–44°, remaining at this temperature from the beginning until the end of the distillation. A mixture of this composition is separated by fractional distillation from an excess of either of its components.

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[1] "On Perchloric Acid and Its Hydrates." Proc. Roy. Soc., **11**, 493 (1862).

[2] "Ueber eine merkwürdige Erscheinung bei der Destillation eines Gemenges von Bromäthylen und Brompropylen." Ann. Supp.-Band, I (1861), p. 250.

[3] "Ueber die Destillation von Gemischen; ein Beitrag zur Theorie der fractionirten Destillation." Ann. Chem. (Liebig), **28**, 328 (1863).

[4] "Sur la Distillation des Liquides melangés." Ann. chim. phys [4], **1**, 384 (1864).

He found the explanation of this phenomenon in essentially physical ideas. If a mixture of two liquids which do not exert any reciprocal action is boiled, both will be volatilized at that temperature at which their united vapor-tensions equal the atmospheric pressure, and in the same ratio by weight as that of the products of their actual vapor-tensions by their vapor-densities respectively. So if the carbon disulphide and alcohol preserved their theoretical vapor-tensions, they would be distilled at about 40° in the proportions of 88.5 parts of carbon disulphide and 11.5 parts of alcohol. But the two liquids exert influence upon each other, as is shown by their mutual solution and by the diminution of the sum of the tensions of their vapors. This influence tends to diminish the individual vapor-tension of each of the liquids, following an unknown law.

5. Ed. Linnemann[1] records three hydrates of isopropyl alcohol (boiling-point 83°–84°, 739 mm.); $3C_3H_8O + 2H_2O$, formed when aqueous propyl alcohol is distilled on the water-bath, boils at 78°–80° (738 mm.), specific gravity 0.832, at 15°; $2C_3H_8O + H_2O$, formed by dehydration with potassium carbonate, boils at 80°; $3C_3H_8O + H_2O$, formed by distilling from anhydrous copper sulphate, boils at 81°, specific gravity 0.800.

6. T. E. Thorp[2] found that a mixture of 1 part methyl alcohol and 3.6 parts carbon tetrachloride boils like a homogeneous liquid about 10° lower than methyl alcohol, the more volatile of the two liquids. Calculation shows that this ratio is almost identical with that obtained by multiplying the vapor-tensions of the two liquids at the temperature of the boiling-point (55.7°) by their respective vapor-densities.

7. D. Konowalow[3] investigated the known mixture of propyl alcohol (boiling-point 97°.4) and water in the ratio of about 77 : 23 parts, which boils at 85°–85°.5. To this composition corresponded the maximum of the curve, whose abscissæ are percentage quantities and ordinates pressures, rep-

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[1] "Untersuchung über die Beziehungen des Isopropyl Alcohols zum Propyl Glycol und zum Glycerin." Ann. Chem. (Liebig), **136**, 40 (1865).

[2] "A Contribution to the Theory of Fractional Distillation." J. Chem. Soc., **35**, 544 (1879).

[3] "Ueber die Dampfspannungen der Flüssigkeitsgemische." Wied. Ann., **14**, 34 (1881).

resenting the vapor-tension of the mixture at a specific temperature.

He found also that a 25 per cent solution of butyric acid (boiling-point 163°) in water boiled constantly at 99°.5. Both of these mixtures change their respective proportions on change of the pressure and temperature of distillation.

8. Ramsay and Young[1] agreed with Konowalow that the mixture of propyl alcohol and water, thought by Chancel to be $C_3H_8O+H_2O$, which distils to the last drop at 87°.5 (738 mm.), is not a definite hydrate. The normal composition of the mixture (71.46 per cent alcohol to 28.54 per cent water) varied with the pressure under which it was distilled.

Apparatus for Distillation under Reduced Pressure.

Mixtures of methyl alcohol and benzene were distilled under different pressures, and the relative amounts of the two liquids contained in the constant boiling portion of the distillates were determined.

The apparatus used to effect fractional distillation, under reduced pressure, was arranged as follows:[2]

A 250 cc. separatory funnel was used as a receiver. This was closed with a two-hole rubber stopper, through which passed the adapter and a branched tube, the latter connecting with the manometer, the exhaust, and the pressure regulator. The last was a glass tube about 800 mm. in length and 20 mm. in diameter, filled to the necessary height with mercury, and closed at the top with a two-hole rubber stopper through which passed a short and a long piece of small glass tubing. The first connected with the receiver and the latter extended below the surface of the mercury a distance corresponding to the desired diminution of pressure. By this means the pressure could easily be kept constant within 10 mm. without interrupting the course of distillation. Successive fractions were drawn off from the funnel into an exhausted receiver, through whose stopper the stem of the funnel passed.

The liquid was distilled from a bulb provided with an additional side tube, connected by rubber and a pinch-cock with a small funnel, into which successive fractions were poured. With caution these could be introduced without diminishing the exhaustion.

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[1] "Note on the Mixture of Propyl Alcohol and Water." Abs. Proc. Chem. Soc., 1888-1889, p. 101.

[2] My thanks are due to Dr. E. E. Reid, of this laboratory, for his kind assistance in designing and constructing this apparatus.

Methyl Alcohol and Benzene.

Method of Analysis.—The distillates were analyzed by the following method :

30–40 cc. of the fraction boiling at a constant temperature were measured off into a burette and a definite proportion of water added. It was found that when alcohol constituted 30–40 per cent of the distillate the water added should be one-third of the volume of the sample. The burette was closed, shaken vigorously, and allowed to stand until the liquid within separated into two sharply divided layers of benzene and aqueous alcoholic solution. The volume of benzene could then be read off and its volume ratio to the alcohol converted into the weight ratio by determining the specific gravity of each liquid.[1]

A series of 6 test determinations of known mixtures gave the following results for the per cent of benzene by volume :

	Per cent of benzene.					
	I.	II.	III.	IV.	V.	VI.
Calculated	58.8	59.5	59.5	60.0	64.0	64.0
Found	58.0	59.4	59.8	60.5	63.5	64.3

Results.—Methyl alcohol (distilled from lime at 64°.5–65°)[2] and commercial benzene (redistilled at 79°–79°.5) were mixed in the proportions by weight, and distilled at the pressures given below. The constant boiling portions analyzed were separated from the excess of either constituent by three fractional distillations in each case.

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[1] The difference between the actual specific gravity of a solution of benzene in methyl or ethyl alcohol and that calculated from the specific gravities of the individual liquids was found by Paterno and Montemartini [Gazz. chim. ital., **24**, II, p. 179 (1894), to be so small (1 or 2 in the third decimal place) that it may be disregarded in this method of determination.

[2] The same thermometer was used throughout this and all succeeding investigations. It had been carefully tested, compared with two standard thermometers, and corrected. Whenever the pressure under which a liquid was distilled is not stated, it was approximately 760 mm.

	Ratio of alcohol to benzene (by weight) in mixture distilled.	Pressure. mm.	Boiling-point of fraction analyzed.	Per cent of alcohol found.	Per cent of benzene found.	Ratio of products of vapor-tension by vapor-density.[1]
I	38 : 62	770	58°	38.4	61.6	At 60°, 37.8 : 62.2
II	38 : 62	760	57°.5–58°	39.0	61.0	
III	37 : 63	400	40°	36.8	63.2	At 40°, 35.2 : 64.8
IV	36 : 64	392	39°.5	35.7	64.3	
V	41 : 59	223	25°	33.2	66.8	At 25°, 33.2 : 66.8
VI	34 : 66	223	25°	33.1	66.9	

Ethyl Alcohol and Benzene.

Mixtures of ethyl alcohol (distilled from anhydrous copper sulphate at 77°.5–78°) and benzene (79°–79°.5) were investigated, and it was found that a mixture containing about 32 per cent of alcohol was distilled to the last drop at 67°–68°.

The results of the analysis of distillates under various pressures, obtained as in the case of methyl alcohol and benzene, are as follows :

	Ratio of alcohol to benzene (by weight) in mixture distilled.	Pressure. mm.	Boiling-point of fraction analyzed.	Per cent of alcohol found.	Per cent of benzene found.	$\frac{\text{v. t.} \times \text{v. d. of alcohol}}{\text{v. t.} \times \text{v. d. of benzene}}$
I	33 : 67	769	67°–68°	31.4	68.6	At 67°.5, 36.3 : 63.7
II	33 : 67	763	67°–68°	32.3	67.7	
III	33 : 67	421	50°–51°	28.2	71.8	At 50°, 32.3 : 67.7
IV	28 : 72	423	50°–51°	27.6	72.4	
V	28 : 72	241	34°.5–35°.5	23.3	76.7	At 35°, 28.9 : 78.1
VI	23 : 77	243	34°.5–35°.5	23.4	76.6	

To determine the percentage composition of the distillates, 40 cc. were shaken with 50–60 cc. of water.

Twelve analyses of known mixtures gave the following results for the per cent of benzene by volume.

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[1] See Berthelot, page 385; and Thorpe, page 386. The values for vapor-tensions throughout these investigations were taken from Landolt and Börnstein's tables, Regnault's values being preferred.

	I.	II.	III.	IV.	V.	VI.
Calculated	60.0	60.0	60.0	65.0	65.0	65.0
Found	59.9	59.9	62.2	65.2	64.8	65.0

	VII.	VIII.	IX.	X.	XI.	XII.
Calculated	65.0	70.0	70.0	70.0	75.0	75.0
Found	66.2	70.1	69.8	70.0	75.0	75.1

General Investigation of the Boiling-points of Binary Mixtures of Liquids Mutually Soluble in all Proportions.

All liquids boiling below 170° that were at hand were purified; and each was mixed with every other whose boiling-point was within 30°–40° of its own, and the mixture distilled. When a constant boiling mixture was found, the ratio of its constituents was determined as nearly as possible by repeated mixing in various proportions, and careful distillation until that ratio was discovered for which the whole mixture distilled most nearly within 1°. A volume of 10–15 cc. was found adequate for each trial mixture distilled.

The ratio of the products of the respective vapor-densities and vapor-tensions at a temperature near that of constant boiling was calculated whenever the necessary data were known, and is given below as the "theoretical ratio."

1. Methyl alcohol (64°.5–65°) and ethyl bromide (37°.5–38°.5) are distilled at 35°–36° (765 mm.) in the approximate ratio of 5 : 95 parts by weight. Theoretical ratio at 35°, 9 : 91 parts by weight.

2. Methyl alcohol and chloroform (60°–61°) at 53°.5–54°.5 (765 mm.); ratio 12 : 88. Theoretical ratio at 55°, 17 : 83.

3. Methyl alcohol and methyl acetate (55°.5–56°.5) at 53°.5–54°.5 (760 mm.); ratio, 18 : 82.

4. Methyl alcohol and ethyl iodide[1] (72°.3–72°.5) at 54°.5–55°.5 (770 mm.); ratio 17 : 83. Theoretical ratio at 55°, 19 : 81.

5. Methyl alcohol and ethyl acetate (75°.5–76°.5) at 61°.7–62°.5 (757 mm.); ratio 47 : 53.

6. Methyl alcohol and benzene. (See p. 388.)

7. Methyl alcohol and isobutyl iodide (118°–119°) at 63°.5–64°.5 (760 mm.). The ratio of 70 : 30 parts by weight gave

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[1] See Wanklyn, page 385.

an excess of alcohol. In this and all succeeding distillations of isobutyl iodide mixtures, the formation of tar made a close determination of the proportions impossible.

Methyl alcohol is separated by fractional distillation from ether (34°.5–35°.5), acetone (56°–57°), and toluene (108°.5–109°.3).

8. Ethyl alcohol (77°.5–78°) and ethyl bromide (37°.5–38°.5) at 36°.5–37°.5 (762 mm.). The theoretical ratio at 37°.5 is 6.6 : 93.4. The actual per cent of alcohol seemed to be about half of the theoretical, but could not be more closely determined.

9. Ethyl alcohol and carbon disulphide[1] (45°.5–46°) at 41°.5–42°.5 (755 mm.); ratio, 9 : 91, verified. Theoretical ratio at 43°–44°, 11.4 : 88.6.

10. Ethyl alcohol and chloroform (60°–61°) at 58°.5–59°.5 (759 mm.); ratio, 6 : 94. Theoretical ratio at 60°, 15.6 : 84.4.

11. Ethyl alcohol and ethyl iodide (71°5–72°.5) at 62°.5–63°.5 (761 mm.); ratio, 14 : 86. Theoretical ratio at 60°, 17.4 : 82.6.

12. Ethyl alcohol and ethyl acetate (75°.5–76°.5) at 71°–72° (765 mm.); ratio, 31 : 69.

13. Ethyl alcohol and benzene. (See p. 389.)

14. Ethyl alcohol and isobutyl iodide (118°–119°) at 76°.5–77°.5 (760 mm.); approximate ratio, 70 : 30.

Ethyl alcohol is separated from propyl alcohol (97°.5) and toluene (108°.7–109°.3).

15. Isopropyl alcohol (81°–82°) and carbon disulphide (45°.5–46°) at 43°.5–44°.5 (761 mm.); ratio, 9 : 91.

16. Isopropyl alcohol and ethyl iodide (71°.5–72°.5) at 65°.5–66°.5 (764 mm.); ratio, 13 : 87.

17. Isopropyl alcohol and ethyl acetate (75°.5–76°.5) at 74°–75° (770 mm.); approximate ratio, 26 : 74.

18. Isopropyl alcohol and benzene (79°–79°.5) at 71°–72° (758 mm.); ratio, 30 : 70.

19. Isopropyl alcohol and water at 78°.5–79°.5 (768 mm.); ratio, 89 : 11.[2]

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[1] See Berthelot, page 385.

[2] See Linnemann, page 386. The per cent of water in the compounds $3C_3H_8O.2H_2O$, $2C_3H_8O.H_2O$ and $3C_3H_8O.H_2O$ is 16.7, 13, and 9 per cent, respectively. The alcohol used by me was distilled from lime at 81°–82°. This case should be investigated further.

20. Isopropyl alcohol and isobutyl iodide (118°–119°) at 81°–82° (761 mm.); approximate ratio, 70 : 30.

Isopropyl alcohol is separated from chloroform (60°–61°) and toluene (108°.7–109°.3).

21. Normal propyl alcohol (95°.7) and ethyl iodide (72°.3–72°.5) at 69°.5–70°.5 (768 mm.) ; approximate ratio, 7 : 93.

22. Propyl alcohol and benzene (79°–79°.5) at 76°–77° (762 mm.) ; ratio, 16.5 : 83.5. Theoretical ratio at 80°, 28.5 : 71.5.

23. Propyl alcohol and water at 87°–87°.5 (770 mm.) ; ratio, 72 : 28.[1] Theoretical ratio at 87°.5, 79 : 21.

24. Propyl alcohol and toluene (108°.7–109°.3) at 91°–92° (765 mm.) ; ratio, 53 : 47.

25. Propyl alcohol and isobutyl iodide (118°–119°) at 92.5°–93°.5 (753 mm.) ; approximate ratio, 45 : 55.

Normal propyl alcohol is separated from ethyl acetate (75°.5–76°.5) and isobutyl alcohol (105°.3–106°.3).

26. Isobutyl alcohol (105°.3–106°.3) and toluene (108.8°–109°.3) at 100° (764 mm.) ; ratio, 43 : 57.

27. Isobutyl alcohol and isobutyl iodide (118°–119°) at 101°–102° (765 mm.). The ratio of 33 : 67 gave an excess of alcohol.

28. Isobutyl alcohol and ethylene bromide (129°–130°) at 104°.5–105°.5 (763 mm.) ; approximate ratio, 62 : 38.

Isobutyl alcohol is separated from ethyl iodide (72°.3–72°.5), benzene (78°.5–79°), and metaxylene (136°–137°).

29. Amyl alcohol (128°–129°)[2] and isobutyl iodide (118°–119°) at 115°–116° (765 mm.). The ratio of 20 : 80 gave a slight excess of iodide.

30. Amyl alcohol and ethylene bromide (129°–130°) at 121°–122° (760 mm.) ; ratio, 30 : 70. Ratio of vapor-densities, 32 : 68.

31. Amyl alcohol and metaxylene (136°–137°) at 125°–126° (760 mm.) ; ratio, 52 : 48. Amyl alcohol and paraxylene (137°–137°.5) at 125°–126°, in the same ratio ; and amyl alcohol and orthoxylene (140°–141°) at 127°–128°, with a slightly larger per cent of alcohol.

[1] See Konowalow, page 386 ; and Ramsay and Young, page 387. My determination of the ratio was made before I knew of that found by Ramsay and Young.

[2] This was obtained by repeated fractionation from the commercial mixture of amyl alcohols.

Amyl alcohol is separated from toluene (108°.8–109°.3).

32. Allyl alcohol (95°–96°) and benzene (79°–79°.5) at 76°–77° (760 mm.). The ratio of 20 : 80 gave a slight excess of alcohol.

33. Allyl alcohol and toluene (108°.8–109°.3) at 91°–92° (756 mm.); approximate ratio, 50 : 50.

34. Acetic acid (117°–118°) and toluene (108°.8–109°.3) at 103°.5–104°.5 (761 mm.); ratio, 30 : 70.

35. Acetic acid and metaxylene (136°–137°) at 113°.5–114°.5 (761 mm.); ratio, 27 : 73.

Acetic acid is separated from carbon disulphide (45°.5–45°.7) and benzene (79°–79°.5).

36. Butyric acid (159°–160°) and water at 99°–99°.5 (763 mm.); ratio, 20 : 80.[1] Theoretical ratio at 100°, 32 : 68.

37. Butyric acid and brombenzene (152°–153°) at 147°–148° (748 mm.); ratio, 19 : 81.

38. Ether (34°.5–35°.5) and carbon disulphide (45°.5–46°) at 34°.5–35°.5 (768 mm.); approximate ratio, 65 : 35. Theoretical ratio at 35°, 59 : 41.

Ether is separated from acetone (56°–57°) and chloroform (60°–61°). A mixture of ether and ethyl bromide (37°.5–38°.5) is distilled at the same temperature (35°–38°) as its constituents.

39. Carbon disulphide (45°.5–45°.7) and ethyl bromide (37°.5–38°.5) at 37°–38° (770 mm.); ratio 32 : 68. Theoretical ratio at 37°.5, 35 : 65.

40. Carbon disulphide and acetone (55°.5–56°.5) at 38°.5–39°.5 (766 mm.); ratio, 74 : 26. Theoretical ratio at 40°, 66 : 34.

41. Carbon disulphide and methyl acetate (55°.5–56°.5) at 39°–40° (756 mm.); ratio, 71 : 29.

42. Carbon disulphide and ethyl acetate (75°.5–76°.5) at 45°.5–46°.5 (768 mm.); ratio, 92 : 8.

Carbon disulphide is separated from chloroform (60°–61°), ethyl iodide (71°.5–72°.5), and benzene (79°–79°.5).

43. Acetone (55°.5–56°.5) and methyl acetate (55°.5–56°.5) in about equal parts are distilled 0°.5 below the boiling-point of either.

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[1] See Konowalow, page 386.

44. Acetone and ethyl iodide (71°.5–72°.5) at 55°–56° (770 mm.); approximate ratio, 60 : 40.

45. Acetone and chloroform (60°–61°) at 64°–65° (760 mm.); approximate ratio, 20 : 80.

Acetone is separated from ethyl bromide (37°.5–38°.5) and ethyl acetate (75°.5–76°.5).

46. Chloroform (60°–61°) and methyl acetate (55°.5–56°.5) at 64°–65° (760 mm.); approximate ratio, 78 : 22.

Chloroform is separated from ethyl bromide (37°.5–38°.5), ethyl iodide (71°.5–72°.5), ethyl acetate (76°–77°), and benzene (79°–79°.5).

47. Ethyl iodide (71°.5–72°.5) and ethyl acetate (75°.5–76°.5) at 69°.5–70°.5 (762 mm.); approximate ratio, 78 : 22.

48. Ethyl iodide and benzene (79°–79°.5) at 74°–75° (758 mm.); approximate ratio, 80 : 20.

Ethyl acetate (75°.5–76°.5) is separated from benzene (79°–79°.5).

Isobutyl iodide (118°–119°) is separated from toluene (108°.7–109°.3).

Acetone (55.°5–56°.5) and benzene (79°–79°.5) in the ratio of 5 : 1 approximately, showed a tendency to gather at 57°–58°, this fraction constantly increasing throughout the course of repeated distillations. But the proportions could not be found for which all of the mixture would boil at this point, as in every case there were small fractions from 57° to 79°.

Ethylene bromide (129°–130°) and metaxylene (136°–137°), in the ratio of 5 : 2 approximately showed a similar tendency to gather at 130°–131°.

Amyl alcohol (128°–129°) and brombenzene (152°–153°), in the ratio of 5 : 2 approximately seemed to be distilled at 128°–129°, but the small per cent of the latter and the formation of tar prevented a definite determination.

Summary.—Of the 80 mixtures examined, 45 were distilled at a constant temperature at or below the boiling-point of the more volatile constituent; 2[1], at a constant temperature above the boiling-point of the less volatile constituent; 1,[2] at a constant temperature between the boiling-points of the constituents; 1,[1] in which the boiling-points of the constituents are too close for fractionation, presents no relative depression or elevation of the boiling-point of the mixture; and 3 are of an uncertain character.

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[1] Nos. 45 and 46.

[2] No. 48.

Boiling-points of Mixtures of Liquids whose Mutual Solubilities are Limited.

Two cases of this kind were examined.

1. Isobutyl alcohol (105°.3–106°.3) saturated with water at the temperature of the room (about 5 parts of alcohol to 1 part of water) boils for a time at the constant temperature of 89°–90°, the distillate separating in the receiver into two layers. The excess of alcohol above the amount necessary for the proportions of distillation at constant temperature causes the temperature to rise gradually to 106°. If the alcohol is saturated at higher temperatures, the portion distilling at 89°–90° is correspondingly larger.

2. Methyl alcohol (64°.5–65°) saturated with carbon disulphide (45°.5–46°) (about equal parts by weight at the temperature of the room) boils for a time at 37°–38°. The excess of alcohol causes the temperature to rise ultimately to 65°. This mixture shows phenomena similar to those noted in case 1.

Conclusions.

1. The large proportion of constant boiling mixtures found in the cases examined makes it evident that this phenomenon is by no means so exceptional as has hitherto been supposed. In fractional distillation one should always be on his guard against it.

2. The changes in the composition of the distillates, corresponding to the changes in pressure and temperature of the distillation, indicate that the two mixtures investigated[2] are not true chemical compounds, and that any approximation to molecular proportions must be regarded as accidental.

3. It is well known that two liquids mutually insoluble are distilled at a constant temperature in the ratio of the products of their respective vapor-densities and vapor-tensions at the temperature of distillation.

[1] Ether-ethyl bromide.

[2] See pages 388 and 389.

If the liquids are partially soluble in each other, they are also distilled at a constant temperature, but with some deviation from this ratio, so long as there are two layers of liquids in the distilling flask.

The results of this investigation are generally in accord with the theory that when two liquids, mutually soluble in all proportions, are distilled at a constant temperature, their ratio in the distillate is that of the products of the vapor-densities and vapor-tensions of the pure liquids at that temperature, modified more or less by their influence upon each other.[1]

Contribution from the Laboratory of General Chemistry, University of Michigan.

THE ACTION OF BENZOYL CHLORIDE ON THE PHENYLHYDRAZONES OF BENZOIN.[2]

BY PAUL C. FREER.

In a previous paper,[3] while discussing the constitution of the phenylhydrazones of benzoin, I described a body, melting at 163°, produced by the action of benzoyl chloride on β-benzoin phenylhydrazone. This substance, owing to analyses and molecular weight determinations in methyl oxalate solution, I presumed to be a third isomeride of the chemical individuals under consideration. The ease with which the reaction takes place (at 0°) and the fact that the benzoyl chloride only in part disappears pointed to this conclusion, but my inability to account for such a body satisfactorily, as well as its appearance, caused me to reinvestigate the entire reaction thoroughly and with large quantities of material. The result was most surprising, for it showed that even at 0° benzoyl chloride accomplishes what I have never before observed with phenylhydrazones; namely, the severance of the two nitrogen atoms in the phenylhydrazine molecule, with the production of benzanilide, which latter substance is the supposed γ-benzoin phenylhydrazone. The two bodies have nearly identical carbon and hydrogen, the difference being in the nitrogen and molecular weight determinations, which the subsequent examination proved to have been in error. The accurate results are very interesting and are consequently given in detail.

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[1] The greatest deviation from the calculated ratio was found in the mixture of propyl alcohol and benzene (No. 22).

[2] This article, which was sent from Germany by the author, reached the editor while the article by Professor Alexander Smith (**22**, 198), calling attention to the same errors, was in press.

[3] This JOURNAL, **21**, 45.

Sixty-five grams of pure β-benzoin phenylhydrazone were dissolved in 350 cc. of dry ether and, after 32.5 grams of pure benzoyl chloride, free from hydrochloric acid, had been added the whole was placed in an atmosphere of carbon dioxide and kept at winter temperature for two days. A slightly pink precipitate weighing 27.5 grams separated out. This was filtered, dried in a current of carbon dioxide, and then thoroughly washed with water until there was no further change; the precipitate then weighed 21 grams, and the water, when neutralized and mixed with the exact amount of silver nitrate, precipitated 8 grams of silver chloride, corresponding to 2.03 grams of hydrochloric acid. The filtrate from the silver chloride was preserved. The original organic precipitate was recrystallized from alcohol and yielded 11 grams of pure benzanilide, identified by its melting-point, molecular weight, combustions, and by its form of crystallization examined, with a sample prepared in another way, according to Lehmann's method with the microscope. The mother-liquors from this recrystallization were then carefully precipitated with water until all of a tarry substance had separated (weight 2.5 grams), and the remainder, after further dilution, was repeatedly extracted with ether, the ether dried and evaporated. There remained a crystalline mass, permeated with some oil, having the odor of benzaldehyde. The crystals were dried on a porous plate and recrystallized from boiling alcohol, in which they were sparingly soluble. These white, feathery needles, melting at 273°–275°, contained 9.6 per cent nitrogen, the calculated amount for $C_{21}H_{17}N_2$ being 9.4 per cent. A comparison of this body with lophine, prepared by the usual method, proved its complete identity. The mother-liquors, after all lophine had been extracted, were evaporated to dryness, leaving 1 gram of a crystalline remainder, which proved to be a mixture of ammonium and aniline salts.

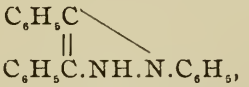
The ethereal filtrate from the original precipitate was evaporated *in vacuo* until nothing but a reddish tar, weighing 67 grams, was left. This was extracted four times with a boiling mixture of one-third ligroin and two-thirds ether. The yellow solution contained all of the unchanged benzoyl chloride and, on evaporation, yielded a mass of needles. These were spread on a porous plate, to remove the liquid impurity, and when dried weighed 19 grams. Recrystallized from alcohol they melted at 96° and were pure benzil, while 3.5 grams of dibenzanilide were obtained from the mother-liquors. The tar, remaining after the above extraction, was then boiled out twice, each time during two hours, with concentrated hydrochloric acid, and then filtered. On standing, the filtrate separated 2.5 grams of benzoic acid and on evaporating it left 7 grams of a crystalline residue. This was extracted with absolute alcohol (the solution turning deep-blue owing to the presence of small quantities of a dye) and the insoluble remainder, tested by the Kjeldahl method, proved to be pure ammonium chloride. The alcohol also extracted a small quantity of the salt of an organic base. There remained unaltered 31.5 grams of a black tar, which was heated to 190° in a sealed tube for several hours with concentrated hydrochloric acid. As a result some more benzoic acid and ammonium chloride was obtained, but 25 grams remained unaltered even at 200°.

The products of the action of benzoyl chloride on β-benzoin phenylhydrazone, in absolute ethereal solution, at winter temperature, are therefore as follows :

The total quantity of phenylhydrazone taken was 65 grams; that of benzoyl chloride was 32.5 grams.

Found.	Grams.
Pure benzanilide	11
Lophine	5
Benzil	11
Dibenzanilide	3.5
Hydrochloric acid	2.03
Ammonium chloride Aniline hydrochloride	1.00
Unchanged benzoyl chloride	8.30
Tar	50.5
Total	94.33

In all other cases in which any crystalline bodies at all have been obtained by the action of benzoyl chloride on phenylhydrazones, these substances have been either mono- or dibenzoylphenylhydrazine or benzoylated phenylhydrazones, but in the case of β-benzoin phenylhydrazone not a trace of these latter products could be discovered. As a consequence, the inference must be drawn that either the body under discussion is not a phenylhydrazone at all or that, by the action of benzoyl chloride, it is first converted into a different substance. The first supposition is scarcely admissible, so that only the second one remains. In order to test this view the action of benzoyl chloride on β-benzoin phenylhydrazone methyl ether was tested. In this case, although a reaction slowly sets in, none of the above products could be obtained, with the exception of some ammonium chloride and traces of benzaldehyde, the remainder being a non-crystallizable tar, and the conclusion that the hydroxyl group is necessary for the above reaction is therefore justified.[1] The first action of benzoyl chloride would therefore be one of dehydration with the production of a body of the structure,



and such a substance could then be decomposed with the separation of an aniline instead of a phenylhydrazine derivative. The nature of the decomposition, whether the benzanilide is the result of hydration and decomposition of the first product of the reaction, or whether it is formed by the addition of benzoyl chloride, as well as the origin of the benzil and lophine, is still undecided, so that the next step in the study of the reaction would be an examination of the action of a substituted benzoyl chloride on β-benzoin phenylhydrazone.

Ten grams of β-benzoin phenylhydrazone and 9 grams of pure *m*-nitrobenzoyl chloride were dissolved in 100 cc. of absolute ether and allowed to stand at winter temperature. After two hours a small quantity of a black tar, apparently an oxidation-product, had separated, and the solution had turned dark-red. This tar was separated, washed with alkali, extracted with ether, and dried; the remainder was non-crystallizable, and only a small quantity of benzil could be obtained from it by extraction with ligroin. The original ethereal solution was once more placed in the cold. After twenty-four hours hard, warty crystals which, when recrystallized from alcohol, melted at 153°, and, on comparison with a product obtained in a different manner, proved to be *m*-nitrobenzanilide were obtained. After the last traces of this body had been formed, the original solution was evaporated in a vacuum, leaving a black tar which had the odor of nitrobenzoyl chloride and, as a result of the presence of this body, was deliquescent. This tar was repeatedly extracted with warm ligroin and the solvent distilled, leaving a crystalline mass. This was covered with a solution of sodium carbonate, to remove unchanged *m*-nitrobenzoyl chloride, and the remainder was then recrystallized from alcohol, and proved to be pure benzil. No lophine, or at least a quantity too small to be identified, could be isolated. The benzanilide and benzil are therefore directly produced by the action of benzoyl chloride on *β*-benzoin phenylhydrazone. The reaction must therefore be one of addition, separation of hydrochloric acid and hydration, the dibenzanilide, of course, being produced by the action of benzoyl chloride on benzanilide. Benzilimide would also result as an intermediary product.

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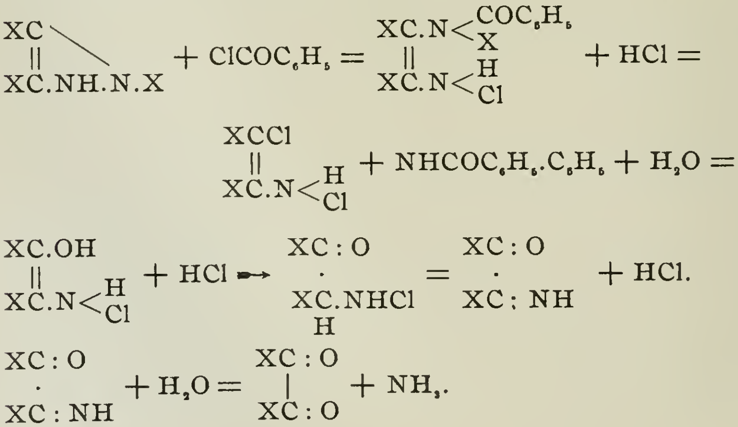
[1] Experiments with desoxybenzoinphenylhydrazone demonstrates that it behaves very differently from the corresponding benzoin derivative. It is an easily oxidized phenylhydrazone, yielding explosive derivatives, and must therefore be classified with the phenylhydrazones of acetone and acetophenone, as a hydrazo obdy.



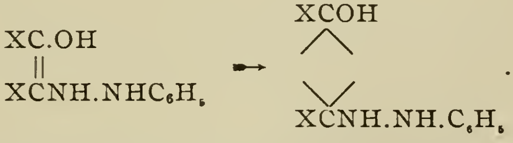
$$\begin{array}{l}XC \diagdown \\ \| \qquad \diagdown \\ XC.NH.N.X\end{array} + ClCOC_6H_5 = \begin{array}{l}XC.N<^{COC_6H_5}_{X} \\ \| \\ XC.N<^{H}_{Cl}\end{array} + HCl =$$

$$\begin{array}{l}XCCl \\ \| \\ XC.N<^{H}_{Cl}\end{array} + NHCOC_6H_5.C_6H_5 + H_2O =$$

$$\begin{array}{l}XC.OH \\ \| \\ XC.N<^{H}_{Cl}\end{array} + HCl \longrightarrow \begin{array}{c}XC:O \\ \cdot \\ XC.NHCl \\ H\end{array} = \begin{array}{c}XC:O \\ \cdot \\ XC:NH\end{array} + HCl.$$

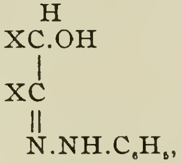
$$\begin{array}{c}XC:O \\ \cdot \\ XC:NH\end{array} + H_2O = \begin{array}{c}XC:O \\ | \\ XC:O\end{array} + NH_3.$$

This series of reactions seems the only way in which to account for the simultaneous production of benzanilide, benzil, and ammonia in about equivalent quantities, the water necessary for the reaction being furnished by the first dehydration. The lophine and tar now remain unaccounted for. The former cannot be produced by a reaction which involves the addition of benzoyl chloride to form a new molecule, otherwise nitrolophine would have appeared among the products of the action of *m*-nitrobenzoyl chloride on β-benzoin phenylhydrazone. The lophine must therefore result directly from the hydrazone, and it can only do so by means of the intervention of benzaldehyde, and the odor of the latter, which is markedly present among the first reaction-products, is proof of its formation. The benzaldehyde is not formed by hydration of β-benzoin phenylhydrazone, for then an equimolecular quantity of benzal phenylhydrazone would result, and none of the latter body could be detected. There seems only one conclusion possible, therefore, and that is the dissociation of the β-benzoin phenylhydrazone with the formation of divalent carbon atoms :



The benzaldehyde with benzil and ammonia in the nascent state would form lophine, while the remainder of the molecule of the hydrazone, in conjunction with benzoyl chloride, would condense to form the tar rather than, by a rearrangement, benzal phenylhydrazone. This accounts for the fact that the tar, on heating with hydrochloric acid, yields benzoic acid, ammonia, aniline, and certain amounts of a blue dye. The only means of explanation for this complex reaction is therefore in the assumption that addition and dissociation reactions take place simultaneously.

As was mentioned in my previous paper, and as I have again convinced myself in this case, α-benzoin phenylhydrazone does not react with benzoyl chloride under the above circumstances ; *i. e.*, at winter temperature. If the difference between the two bodies is one of geometric isomerism, and if they are both true phenylhydrazones this fact could be easily explained by the assumption that the β-hydrazone is the *cis* modification in regard to the hydroxyl group,



$$\begin{array}{l} \quad\;\, H \\ XC.OH \\ \quad\;\, | \\ XC \\ \quad\;\, \| \\ \quad\;\, N.NH.C_6H_5, \end{array}$$

while the α is the *trans.* The formation of benzil, benzanilide, and lophine cannot, however, be explained with this formula as a basis, without assuming extensive intramolecular changes. I was surprised, however, to discover that *m*-nitrobenzoyl chloride reacts with α- in exactly the same way as it does with β-benzoin phenylhydrazone. With either theory as a basis, this behavior can only be explained by the assumption that the more reactive nitro chloride is able to transform the α-into the β-body, but as the latter would inevitably be destroyed by the nitrobenzoyl chloride which is present, no absolute proof of this can, of course, be furnished.

The best proof of the hydrazo structure of β-benzoin phenylhydrazone at present rests upon the fact that it yields the red nitrogen trioxide addition-product and the perbromide of the latter, described in my previous paper, but unless the azo derivative, similar to the ones obtained by me from other hydrazones, can be isolated, a definite decision in either direction cannot be reached.

MUNICH, August, 1899.

Contribution from the Kent Chemical Laboratory of Yale University.

NOTES ON THE SPACE ISOMERISM OF THE TOLUQUINONEOXIME ETHERS.

BY WM. CONGER MORGAN.

In an article on the "Ethers of Toluquinoneoxime and their Bearing on the Space Isomerism of Nitrogen,"[1] published from this laboratory, it was stated that the methyl, acetyl, and benzoyl ethers of toluquinonemetaoxime, whether formed by the action of hydroxylamine on the quinone or by nitrous acid on the corresponding cresol, showed evidence of existing in isomeric forms. Of these bodies the benzoyl ether received the most careful investigation, and by fractional crystallization, from the crude reaction-product, two portions were obtained, one readily separating from an alcoholic solution in the form of yellow crystals melting at 193°, while a second body, melting approximately at 144°, was never obtained in a state of purity. The fact that from this lower-melting fraction, on recrystallization, a portion of the higher-melting body was always obtained, suggested the possibility that the solvent might have a tendency to cause a transition from one isomer to the other. Since, however, after repeated crystallizations from boiling alcohol a low-melting fraction was obtained, and therefore such rearrangement was evidently incomplete, the action of alcohol under pressure on the different fractions was investigated. From a portion of the ether melting at 139°, heated for three hours in a closed tube to 120°, the product melting at 193° crystallized in a characteristic form and no crystals were obtained melting lower than 180°. On treating the higher-melting isomer in the same way, no action was observed until the temperature was raised above 150°, when complete decomposition ensued.

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[1] Bridge and Morgan : This JOURNAL, **20**, 761.

In order to ascertain, if possible, a direct method of transition from one form into the other, the action of alkalies, among other reagents, was tried. No change other than a hydrolytic cleavage was observed, and this was readily completed on warming. By saponifying a fraction melting completely at 142° and treating the isolated oxime in the usual way with benzoyl chloride, the benzoyl ether was again obtained, liquefying at 193°, and, although there was a trifling irregularity in the melting-point of some of the crystals, no low-melting fraction was isolated. On similar treatment of a portion melting at 193° the original ether was obtained, but none of the low-melting isomer.

From these facts it is obvious that the isomer existing in a much smaller proportion in the crude reaction-products, present as the principal constituent in the low-melting fractions, must be regarded as the labile form, tending to go over into the stable form under the influence of boiling alcohol or during the process of a chemical reaction. This action of alcohol increases the difficulty of isolating the labile form and naturally suggests the idea of using other solvents; but imperfect as was the separation of the two isomers, better results were obtained from an alcoholic solution than by any other means.

The phenomena described in the article to which reference was previously made, have been reproduced completely in the ethers made by the action of acid chlorides on the sodium salt of the oxime (to be described later) produced by the action of pure amyl nitrite on the sodium salt of the cresol. In the resulting metathesis, as in the product of the reaction of hydroxylamine on the quinones, there is not the possibility of the formation of a nitro body as there is in the action of free nitrous acid on the cresols. Consequently the interfering action of an admixture of such a body with the oxime ethers cannot influence the results as obtained, yet the presence of a low-melting body existing in a larger proportion in this product than in the substances formed by the agency of free nitrous acid according to the type fraction, was indisputably evidenced. The identity of the observed phenomena under varying conditions and methods of formation, thus removing the probability of an admixture of an impurity and at the same time of a structural difference, seems to establish the hypothesis of a space isomerism in the case of the ethers of toluquinonemetaoxime.

Inasmuch as the monohalogen derivatives of the quinoneoxime ethers are beautifully crystalline bodies, it was thought advisable to prepare the monochlor- and monobrombenzoyl ethers of toluquinoneorthooxime in the hope of obtaining from these well-characterized products additional evidence as to the existence of isomeric phenomena in the orthooxime ethers. Although there was the possibility of both "space" and "place" isomerism neither body offered any indication of the presence of isomers of any kind, but each appeared to be an entirely homogeneous and simple substance, liquefying sharply at a definite melting-point.

EXPERIMENTAL PART.

The Sodium Salt of Toluquinonemetaoxime.

The sodium salt was prepared according to the general method suggested by Walker.[1] To a molecule of sodium alcoholate freshly prepared by dissolving metallic sodium in as little alcohol as possible, a molecule of the orthocresol was added and the solution treated with slightly more than the theoretical quantity of amyl nitrite, the whole being thoroughly mixed together. On standing in a vacuum over sulphuric acid, the sodium salt separates in fine purple crystals, which, on washing carefully with ether to remove amyl alcohol and excess of nitrite, is ready for use. It may be recrystallized from dilute alcohol if further purification is desired. This salt is extremely soluble in water, much less in alcohol, and insoluble in most other organic liquids. On standing in the air it tends to decompose, turning almost black. On analysis:

0.1231 gram, dried over H_2SO_4, gave 0.0541 gram Na_2SO_4.

	Calculated for $C_7H_6O_2NNa$.	Found.
Na	14.48	14.26

Monobromtoluquinone-o-oxime Benzoyl Ether.

This ether was obtained from the dibromide previously described[2] by boiling with dilute 75 per cent alcohol, during which process hydrobromic acid is split off. Being much less soluble in alcohol than the dibromide, the monobrom body separates from the solution as soon as formed and may be obtained as a yellow crystalline powder by filtration of the cooled liquid. On analysis,

0.1450 gram, dried over H_2SO_4, gave 0.2774 gram CO_2, and 0.0415 gram H_2O.

0.1102 gram gave 0.0643 gram AgBr.

	Calculated for $C_{14}H_{10}Br.NO_3$.	Found.
C	52.49	52.17
H	3.15	3.18
Br	24.98	24.83

On crystallizing from alcohol the ether was readily obtained in two, apparently unlike, modifications, one being long prismatic crystals, the other appearing as broad, thick, monoclinic plates. It was at first believed that this distinction in crystal form was due to the presence of isomeric bodies, but no difference in melting-point could be found since each portion liquefied sharply at 184°. Under the lens, moreover, the plates are seen to be striated parallel to one edge and have all the appearance of consisting of a number of the simple crystals united to each other, since both forms are plainly of the same system. Slow cooling was found to be productive of the massed crystals.

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[1] Walker: Ber. d. chem. Ges., **17**, 399.

[2] Bridge and Morgan: This JOURNAL, **20**, 776.

Toluquinone-o-oxime Benzoyl Ether Dichloride.

The benzoyl ether was dissolved in a small amount of chloroform and dry chlorine gas passed into the solution. The action is very rapid and after fifteen minutes the liquid may be allowed to evaporate and the white product, crystallized once from glacial acetic acid, melts sharply to a colorless liquid at 149° without decomposition. Fractional crystallization does not change the melting-point except as the action of the solvent causes a slight formation of the monochlor body. On analysis,

0.1241 gram, dried over H_2SO_4, gave 0.2431 gram CO_2, and 0.0424 gram H_2O.

0.2105 gram gave 0.1930 gram AgCl.

	Calculated for $C_{14}H_{11}Cl_2NO_3$.	Found.
C	53.84	53.42
H	3.55	3.80
Cl	22.72	22.67

The dichloride, like the dibromide, is slightly soluble in alcohol, readily soluble in chloroform, glacial acetic acid, and fuming nitric acid. Water precipitates the ether entirely unchanged from the two last-mentioned solvents. In crystal form it resembles very closely the dibromide, separating from a boiling acetic acid solution in short, thick, colorless, almost microscopic prisms, suggesting the orthorhombic system. In point of stability this ether, as well as the monochlor body, far surpasses the corresponding bromine compounds.

Monochlortoluquinone-o-oxime Benzoyl Ether.

Analogous to the dibromide, by the action of dilute alcohol on the dichloride, hydrochloric acid is split off and a yellow monochlor substitution-product is formed, one hour being sufficient to complete the reaction. This ether closely resembles the monobrom derivative in properties and in crystal form. The product as obtained from an alcoholic solution will decompose and melt at a temperature varying ordinarily from 185°–193°, depending on the rapidity with which the heat is applied. "Dipped" for fifteen seconds, the crystals melt without decomposition at 200°. Although carefully fractioned from alcohol, ligroin, and benzol, the substance appeared to be entirely homogeneous, and no variation in the melting-point was observed. On analysis,

0.1209 gram, dried over H_2SO_4, gave 0.2688 gram CO_2, and 0.0424 gram H_2O.

0.1035 gram gave 0.0533 gram AgCl.

	Calculated for $C_{14}H_{10}Cl.NO_3$.	Found.
C	60.97	60.63
H	3.66	3.90
Cl	12.87	12.75

JUNE, 1899.

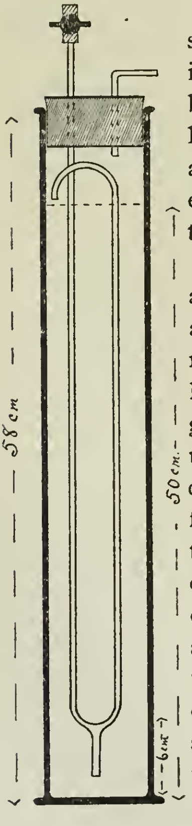
A DISSOLVER.

BY ARTHUR JOHN HOPKINS.

An apparatus for hastening the solution of salts has been described by Richards.[1] That such devices will supplant the good old methods of heating or stirring is not to be supposed; but heating is often proscribed by the nature of the salt or the requirement of a constant temperature, and stirring by hand is laborious and inconstant; and although both constant temperature and constant circulation are supplied by mechanical stirrers, yet it is possible that the necessity for mechanical devices has deterred many a chemist from entering upon the study of solubilities. A field may therefore be open for an apparatus serving the same purpose as a stirrer and constructed from material with which the chemist is already familiar.

[1] This JOURNAL, 20, 189.

Richards' dissolver, although of simple construction, is very efficient and moreover is automatic, in that it requires no stirrer. Its efficiency is obviously limited to such salts as can form saturated solutions of much greater specific gravity than the solvent and further limited to the formation of non-saturated solutions of these salts. The rate of flow in a purely automatic dissolver will rapidly approach zero, as the specific gravity of the solvent gains on that of the saturated solution. In fact, at any one moment the rapidity of solution varies as the square of the velocity of the solvent passing the crystals.



In the hope of making a dissolver which shall be universally applicable without resorting to mechanical stirrers, an attempt has been made in this laboratory to apply a well-known device to this problem. The result is a dissolver of simple construction and great efficiency, which will rapidly prepare solutions of any specific gravity.

The accompanying illustration shows such an apparatus. An ordinary glass cylinder of any convenient size may be used. The one represented holds 2200 cc.[1] Through one hole of a two-holed stopper is passed a straight glass tube of about 6 mm. bore, fitted at the upper end with a short rubber tube and screw-cock. The lower end of this glass tube is fused, or bound by aid of rubber connection tubing, to one arm of a Y-tube, the lower arm of which reaches nearly to the bottom of the cylinder. The third arm of the Y-tube meets a second glass tube, which reaches up nearly to the stopper and there curves down to give direction to the concentrating solution. The second hole of the stopper carries a short exit tube bent at a right angle, the lower portion of which extends to a point just below the bottom of the stopper.

To use the dissolver, introduce the desired quantity of water or other solvent with the weighed quantity of salt to be dissolved, then put the stopper, carrying its tubes, firmly into position, and apply, by means of a filter-pump attached to the short right-angled tube, enough suction to overcome the water pressure of 44 cm. A current of air, regulated by the screw-cock to prevent vibrations in the Y-tube, follows the water down the long tube in continuous column, but continues only as far as the junction of the Y-tube, for there it is broken into little columns alternating with columns of the saturating solution drawn up through the lower arm of the Y-tube. These broken columns of air, rising through the curved tube, lift the solution drawn directly from the crystals, and throw it out upon the least saturated solvent at the top. The air escapes through the short tube, and the fresh solvent, which occupied the upper position in the cylinder at the beginning, sinks down to dissolve more of the crystals below. When a carefully regulated and not too great suction is applied, there is a continuous and rapid current of the solution passing the crystals while the saturated solution may be seen streaming from the crystals to the lower end of the Y-tube.

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[1] It is best to choose a cylinder of such size that the quantity of solution desired shall fill it to a point just below the curved tube.

To test the efficiency of this apparatus, 30 grams of copper sulphate in crystals of about 2 grams each were dissolved in 200 cc. of distilled water at 19°. For this purpose a cylinder of about one-tenth the size described was selected. Complete solution took place in about forty minutes.

In order to prepare a solution of ammonium carbonate for use in qualitative analysis, a very large stand-cylinder which had formerly served as a generator of hydrogen sulphide, was employed. The proper tubes were attached to the stopper and when 1 kilo of commercial ammonium carbonate, 1 liter of concentrated ammonium hydroxide, and 4 liters of distilled water had been placed in the stand-glass, suction was applied, and in thirty minutes all but about 20 grams of the salt had been dissolved. Dissolving this salt in such large quantities by the usual method takes not less than four or five consecutive hours, and in busy laboratories a day or two of intermittent stirring is often allowed. Assembling the parts of the apparatus and affecting the solution, in the case cited, required less than forty-five minutes.

This dissolver has been used, in a bath of constant temperature, for making saturated solutions of copper sulphate and for determining the solubility of this salt at different temperatures. For this purpose the lower end of the short reduction tube was protected and the entering air was washed through caustic potash and then through sulphuric acid, and again washed on leaving through weighed sulphuric acid tubes. Completely saturated solutions were obtained in about ninety minutes. This work will be taken up again in this laboratory and reported upon.

The dissolver here described, like that of Richards, requires no attention and is very easily constructed in a few minutes from ordinary laboratory material. It involves no mechanical difficulties, is universally applicable, and seems as rapid as any of the mechanical stirrers or shakers.

AMHERST COLLEGE, 1899.

OBITUARY NOTICES.

EDWARD FRANKLAND.

The deaths of Bunsen and Frankland, both of which have occurred during the summer, have left a sad vacancy in the ranks of those who were so active about the middle of the century, during a critical period of the development of the science of chemistry, the formative period of its theories. Frankland, who was born Jan. 18, 1825, died August 9th, in Norway, where he was accustomed to spend his summers. Although in his seventy-fifth year his vigor and activity made him appear much younger. After being educated at the Grammar school of his native town and acting as one of the science masters at Queenwood College, he went to Germany and came under the influence of Liebig and Bunsen. In 1851 he returned to England and was appointed professor at Owens College, Manchester, which place he left in 1857 to take charge of the chemical department of St. Bartholomew's Hospital Medical School in London. In 1863 he was appointed Fullerian professor of chemistry in the Royal Institute and in 1865 succeeded Hofmann in the chair which was afterwards transferred to the Royal School of Mines at South Kensington. He occupied this position until he retired in 1885. He was honored by election to membership in many societies at home and abroad, was president of the Chemical

Society in 1871–72, foreign secretary of the Royal Society for the past five years, and received the Copley medal in 1894. He was knighted in 1897 for his activity as water analyst for more than twenty years. Following the example of Liebig and others, who were at that time vigorous supporters of the radical theory, Frankland attempted to isolate the much sought for radicals. He obtained a product which he considered to be the radical C_2H_5, but which was shown later to be C_4H_{10}. Shortly afterwards, in a paper entitled "On a New Series of Organic Compounds containing Metals" he describes the organo-metallic compounds. According to the views of Kolbe, which were widely accepted at that time, all organic compounds could be explained as copulated radicals, an explanation, however, that was not satisfactory even to Kolbe. Frankland soon recognized that the organo-metallic compounds could not be explained in this way, but that each element had a saturating capacity as regards other elements. He found that these ideas of the definite saturating capacity of elements could be applied to both inorganic and organic compounds, and Kolbe recognized the value of these ideas and modified his ideas of copulae to conform to the views as expressed by Frankland, who said that "no matter what the character of the uniting atoms may be, the combining power of the attracting element is always satisfied by the same number of these atoms." He recognized that the atoms of the metals and metalloids, in their power of uniting with the radical of alcohol, with halogens and oxygen possessed a varying but, within certain limits, definite saturating capacity. These ideas, in which we find the first clear view of our present theory of valence, were very slowly accepted, and it was not until the appearance of Kekulé's papers "On the Constitution of Chemical Compounds" that their value was recognized. The quadrivalence of carbon, which is so often claimed to have originated with Kekulé, had already been recognized by Kolbe and Frankland, and it was the suggestion as to "the linkage of atoms" for which we are especially indebted to Kekulé. Since his appointment, in 1863, as a member of a Royal Commission on the Pollution of Rivers and Domestic Water Supply, Frankland has been greatly interested in this subject and has been one of the greatest authorities on the analysis of drinking-water. J. E. G.

ROBERT WILHELM BUNSEN.

The chemists of the whole world, and especially the elder ones who were so fortunate as to come in personal relationship with Bunsen, will regard his death, which occurred August

16th, as a personal grief, for not only was he respected and looked up to as a great investigator, but he was loved as a teacher and a friend. His wonderful skill in experimenting and his genius which was so strongly manifested in his patient teaching endeared him to many who came under his influence. His simple and unpretentious manner made him a great favorite in the university life at Heidelberg. He spent his life in a university atmosphere as his father was a distinguished Göttingen professor. Born in 1811, he graduated as a Ph.D. at Göttingen in 1831. The next five years he spent in studying in Paris, Berlin, and Vienna, and in 1836 succeeded Wöhler at Cassel. From there he was called to Marburg, then to Breslau, where he only remained a short while before he was called to become professor at Heidelberg, to remain one of that university's distinguished faculty until his resignation in 1889. The first work to which our thoughts turn, when his name is mentioned, is that on the organic compounds of arsenic, now regarded as one of the classics of chemistry. His work, in conjunction with Kirchhoff, on spectrum analysis, was probably his greatest contribution to science. These researches opened up an entirely new field of chemistry, for not only could very small quantities of the known elements be easily detected by these methods, but unknown elements could be detected by its aid, as Bunsen and Kirchhoff showed shortly afterwards when they discovered cesium and rubidium, elements so similar to potassium and sodium that they had previously been mistaken for them ; and, as has been more recently shown, in connection with the discovery of argon, helium, and other gases occurring in the atmosphere. Through the aid of spectrum analysis not only the composition of the stars but even the nature of their motion can be determined. The methods for the detection and estimation of gases as devised and arranged by him have been found so precise and thorough that only trifling changes have been made in them. His work on the geological conditions of Iceland and on geysers and volcanic rocks led to very important new views on this subject. It was only after the work of Bunsen and his followers on the nature of the gases and products formed in an explosion of gunpowder that the nature of the process was understood, and his work on furnace gases led to a much clearer insight into the chemical processes taking place there. These lines of investigation, besides such as his important study of the chemical action of light and of specific heats, are sufficient to show what an impetus Bunsen gave to every line of investigation which he undertook. To the world at large he is perhaps best known as the designer of the burner and battery which bear his name. He was the author of a number of scientific works and a member of many scientific societies. He was awarded the Copley medal in 1860, and in 1877 was, jointly with Kirchhoff, the first recipient of the newly-instituted Davy medal. With the exception of his eyesight, which was slightly impaired, he retained his faculties to the end. J. E. G.

REVIEWS.

The Fundamental Laws of Electrolytic Conduction. Edited by H. M. Goodwin, Ph.D. Harper and Brothers. 1899.

This is one of Harper's Scientific Memoirs now being published under the editorial supervision of Professor J. S. Ames, of the Johns Hopkins University. The general scope of the series has already been outlined in this Journal, **21**, 539. The present volume contains reprints of the papers entitled "Relation by Measure of Common and Voltaic Electricity," and "On Electrochemical Decomposition," by Michael Faraday; and translations of the following papers, "On the Migration of Ions during Electrolysis," by W. Hittorf and "On the Conductivity of Electrolytes Dissolved in Water in Relation to the Migration of their Components," by F. Kohlrausch. The book also contains the usual biographical sketches of the authors of the papers and a bibliography of the most important articles pertaining to these subjects.

J. E. G.

The Rise and Development of the Liquefaction of Gases. By Willett L. Hardin, Ph.D. Harrison Senior Fellow in Chemistry in the University of Pennsylvania. New York. The Macmillan Company. 1899. 250 pages. $1.50.

This book will be very acceptable to those, and there are many such, who have occasion to study the history and development of the liquefaction of gases. The great interest in this subject, that has been aroused by the preparation of liquid air in large quantities and the liquefaction of those gases which have for so long resisted all attempts in that direction, has given rise to numerous articles on this subject written in a popular style. Much of the material is contained in journals not accessible to the general reader and the author has collected and arranged it in the form of a connected chronological treatise. After a general treatment of the historical and theoretical side of the problem, the experiments of Cailletet and his successors are described in detail with diagrams of the apparatus used. The author wisely refrains from any expression of opinion on the Dewar-Hampson-Linde-

Tripler priority claims. While the book is written in a popular-science style, sufficient details are given for all purposes except those of the specialist and he will probably have access to the original articles, to which full references are given. The book is thoroughly up to date and contains the results of work done up to April 1899.

J. E. G.

GRUNDRISS DER ALLGEMEINEN CHEMIE. VON W. OSTWALD. Mit 57 Textfiguren, Dritte, Umgearbeitete Auflage. Leipzig: Verlag von Wilhelm Engelmann. pp. 549. 1899.

The earlier editions of Ostwald's "Grundriss" have done more to arouse an interest in the elements of physical chemistry, than any book ever written. This applies not alone to readers of German, since we have been so fortunate as to have at our disposal an admirable English translation by Dr. Walker. The third edition has been prepared for the purpose of incorporating the work of the last ten years. It has been rearranged and enlarged, until it almost amounts to a new book, changes and additions having been made at every turn.

The new edition, like the old, is divided into twelve books, but the order is by no means the same. Book one, deals with mass; the conservation of mass, the laws of definite and multiple proportions, the conception of an element and atomic weights, including most of the recent atomic weight determinations, and the relations between the atomic weights as brought out by the periodic system. Books two, three, and four, are on the stöichiometry of gases, liquids, and solids, respectively. Book five, on dilute solutions is, of course, of special interest. Chapters are devoted to osmotic pressure, diffusion, vapor-pressure of solutions, freezing-point of solutions, and salt solutions. The Beckmann boiling-point and freezing-point apparatus, should always be given a prominent place in connection with these methods, because these are the forerunners of all that has been done. But both of these methods, and especially the apparatus used in carrying them out, have been so greatly improved, that it would seem that the value of these chapters would have been increased by a brief reference to the newer work.

Book seven, on systematics, contains chapters on the choice of combining weights, the periodic law, the molecular theory, and the theory of chemical compounds. These seven books constitute the first part of the volume, which, as a whole, is known as *stöichiometry*.

The second part of the volume, on *affinity*, takes up the various energy transformations, and includes book seven, on thermochemistry, book eight, on chemical mechanics, book nine, on electrochemistry, book ten, on photochemistry, and book eleven on methods of measuring chemical affinity.

There is, perhaps, no portion of the work as much enlarged as that which deals with electrochemistry. This is due to the unusual activity which has manifested itself in this field during the past few years. The order of treatment here, is very much the same as in the *Lehrbuch*: The law of Faraday, conductivity, properties of ions and electromotive force of elements. A chapter has also been introduced on electrical equilibrium.

In this third edition of the "Grundriss," we are provided with an elementary treatise, covering the whole field of physical chemistry. The work needs no comment, since it comes from the one who has done more than all others to systematize the newer developments, and found the modern school of physical chemistry. An English translation of the book would be welcomed by those who are not familiar with German.

H. C. J.

OUTLINES OF PHYSICAL CHEMISTRY. BY A. REYCHLER, Professor of Chemistry in the University of Brussels. Translated from the French, with the Author's permission, by John McCrae, Ph.D., Demonstrator of Chemistry, The Yorkshire College, Leeds. With 52 Illustrations. Whittaker and Co., London. Macmillan, New York. pp. 271. 1899.

The large number of elementary books upon one chapter or another of physical chemistry, is but an expression of the growing interest in this branch of science. Among these, the little book in hand deserves a prominent place. The subject is treated in a much broader way than is common in an elementary work, and a sharp feeling for the relative importance of things is manifested throughout.

The book begins with a reference to the fundamental laws of chemical action and the laws of weight, and of definite and multiple proportions, and this is followed by a brief discussion of the density of gases, and methods for determining their molecular weights. A short account of the constitution of molecules and of Mendeléeff's classification of the elements is given, and then chapters follow on the stöichiometry of gases, liquids, and solids. The third part of the work deals with thermochemistry, electrochemistry, and the nature of salt solutions. The fourth and last takes up problems in chemical equilibrium, chemical dynamics, and hydrolytic dissociation.

We notice that in a few places the more recent work is not mentioned. Under the refracting power of liquids no mention is made of the work of Edwards. In the interesting chapter on optical activity and the Le Bel-van't Hoff hypothesis, the unique exception discovered by Baeyer should find a place.

The work of Rodger and Watson on magnetic rotation is of the highest importance, and should, at least, be ranked with that of Perkin. The freezing-point and boiling-point methods, devised by Beckmann for determining molecular weights, have been so far improved, that the original forms are hardly used at the present, and these methods have both been applied to a problem of greater interest and importance than that of determining molecular weights; *viz.*, the measurement of the dissociation of electrolytes in aqueous and non-aqueous solutions.

But it is impossible to include everything in a small, elementary, treatise, and we are impressed rather with the large amount of interesting and important material in this little treatise, than with the few omissions. The book is unusually clear and concise, and is very well illustrated. It is heartily recommended to any one who wishes to begin the study of physical chemistry.

H. C. J.

INDICATORS AND TEST-PAPERS. Their source, preparation, application, and tests for sensitiveness. A résumé of the current facts regarding the action and application of the indicators and test-papers which have been proposed from time to time, and are in present use in chemical manipulations. By ALFRED I. COHN, PH.G. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1899. 249 pages. Cloth, $2.00.

The author has collected from all available sources the list of substances which have been suggested for use as indicators and test-papers and has arranged them in this book, the general nature of which is expressed upon the title-page.

J. E. G.

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SOME DOUBLE HALIDES OF CADMIUM WITH THE METHYLAMINES AND TETRAMETHYLAMMONIUM.[1]

BY C. D. RAGLAND.

The results obtained in investigations of the double halides formed by halides of the heavy metals and those of ammonium led to experiments with substituted ammonias, and the work of Slagle[2] and Base,[3] with aniline and the toluidines, has been extended in this investigation to a study of the compounds formed by the methylamines and tetramethylammonium. The following double halides of cadmium with the halides of the alkali metals and ammonium are recorded in the literature.

1 : 1	2 : 1
$(NH_4)CdBr_3,\frac{1}{2}H_2O$	$(NH_4)_2CdCl_4,H_2O$
NH_4CdF_3	$(NH_4)_2CdI_4,2H_2O$
$NaCdBr_3,2\frac{1}{2}H_2O$	$Na_2CdCl_4,3H_2O$
$KCdCl_3,\frac{1}{2}H_2O$	K_2CdCl_4
$KCdBr_3,\frac{1}{2}H_2O$	K_2CdCl_4,H_2O
$CsCdCl_3$	$Na_2CdI_4,6H_2O$
$CsCdBr_3$	$K_2CdI_4,2H_2O$
$CsCdI_3,H_2O$	Cs_2CdCl_4
	Cs_2CdBr_4
	Cs_2CdI_4
	Rb_2CdCl_4

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[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1897. The work was undertaken at the suggestion of Professor Remsen, and was carried on under his guidance.

[2] This JOURNAL, **20**, 633.

[3] *Ibid.*, **20**, 646.

3 : 1	4 : 1
Cs_3CdBr_5	$(NH_4)_4CdCl_6$
Cs_3CdI_5	$(NH_4)_4CdBr_6$
	K_4CdCl_6
	K_4CdBr_6

Preparation of Material.

Cadmium chloride and cadmium iodide were prepared by dissolving the metal, previously tested for purity, in the respective acids and evaporating the solutions to dryness.

Inasmuch as cadmium dissolves quite slowly in hydriodic acid, in a subsequent preparation of the iodide, cadmium oxide was used. This was prepared by igniting the oxalate, which was precipitated from a solution of cadmium nitrate by oxalic acid. Cadmium bromide was prepared first by heating the metal in a combustion tube and passing bromine vapor over it, the bromide subliming to the cooler part of the tube. However, it was found later to be more convenient to dissolve the metal in bromine water. The bromine in both cases was purified by distillation from potassium bromide.

The hydrochlorides of the methylamines (Bender and Hobein's preparations) were used as the sources of the bases.

Tetramethylammonium hydroxide was prepared from the iodide by Hofmann's original method.[1] A moderately dilute solution of the iodide was gently warmed, and shaken up with moist silver oxide until further additions of the dark-brown oxide were no longer changed to the yellow silver iodide. The solution was then filtered and afterwards found to be free from iodine.

The bases were neutralized with the required acids, and the solutions were then concentrated to a convenient bulk.

Methods of Analysis.

The objections which Muspratt[2] raises to the established method of determining cadmium were not confirmed by my experience.

Preliminary experiments were made in which cadmium, known to be very pure, was used. A weighed quantity was dissolved in hydrochloric acid and the solution was diluted to a known volume. Portions were drawn off and analyzed. In every case the analyses were perfectly satisfactory.

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[1] Ann. Chem. (Liebig), **78**, 263.

[2] J. Soc. Chem. Ind., **13**, 211.

The method used in determining cadmium was as follows: Dilute solutions were heated to a temperature near boiling, and a strong solution of potassium carbonate was added, drop by drop, with constant stirring. After boiling a few minutes and allowing the beaker to stand, the whitish translucent precipitate of basic cadmium carbonate settled to the bottom, leaving the supernatant liquid perfectly clear.

A Gooch crucible was used in all cases for filtration. After washing several times by decantation, the precipitate was thrown on the filter and washed with several hundred cc. of boiling water. The Gooch crucible, without a cap, was then placed on a platinum plate in an iron crucible, dried at a moderate heat, and heated to dull redness for ten or fifteen minutes.

The halogens were determined by the volumetric methods of Mohr and Volhardt, and gravimetrically. When the silver halides were weighed, a Gooch crucible was used, and the precipitate was dried in an air-bath at 140°.

Preparation of the Double Salts.

Concentrated solutions of the two salts were made, and from the calculated amounts present in each, such volumes of the two solutions were taken as to vary the molecular proportions in the different beakers, thus:

1 : 1; 1 : 2; 1 : 3; 1 : 4; 2 : 1; 3 : 1; 4 : 1.

Other proportions were used in cases which seemed to justify the use of solutions of greater proportional difference. The mixtures were acidulated with the corresponding acid, and put in vacuum desiccators over sulphuric acid and caustic soda. The successive crops of crystals were analyzed as long as they appeared homogeneous. The microscope was constantly used to ascertain this.

Further particulars will be noted in the descriptions of the individual double salts.

Compounds Described.

2 : 1 Methylamine chlorcadmiate.
1 : 1 Methylamine bromcadmiate.
2 : 1 Methylamine bromcadmiate.
1 : 1 Dimethylamine chlorcadmiate.
1 : 2 Dimethylamine chlorcadmiate.
3 : 2 Dimethylamine chlorcadmiate.
1 : 1 Dimethylamine bromcadmiate.
2 : 1 Dimethylamine bromcadmiate.
1 : 4 Dimethylamine bromcadmiate.
1 : 1 Dimethylamine iodocadmiate.
1 : 1 Trimethylamine chlorcadmiate.
3 : 2 Trimethylamine chlorcadmiate.
1 : 1 Trimethylamine bromcadmiate.
3 : 2 Trimethylamine bromcadmiate.
1 : 1 Trimethylamine iodocadmiate.
2 : 1 Trimethylamine iodocadmiate.
1 : 1 Tetramethylammonium chlorcadmiate.
1 : 1 Tetramethylammonium bromcadmiate.
2 : 1 Tetramethylammonium bromcadmiate.
1 : 1 Tetramethylammonium iodocadmiate.
2 : 1 Tetramethylammonium iodocadmiate.

METHYLAMINE SALTS.

Double Chlorides.

2 : 1 Methylamine Chlorcadmiate.—When solutions of cadmium chloride and methylamine hydrochloride are mixed so that the number of molecules of the former to that of the latter bear these ratios: 2 : 1; 1 : 1; 1 : 2; 1 : 3; 1 : 4; the same double salt crystallizes out in every case.

Usually three or four successive crops of crystals from each beaker were obtained. The crystals are tabular, transparent, with a fibrous fracture, resembling selenite in general appearance. The cleavage is perfect, parallel to the broad faces, giving thin, pearly, flexible laminae.

Unsuccessful efforts were made to get specimens for crystallographic work. The general appearance of the crystals would indicate that they are isometric in form.

The solutions from which these crystals were obtained were very concentrated. The mother-liquor was drained off as thoroughly as possible, and the crystals quickly washed with water, pressed between layers of smooth drying-paper, and dried in the air.

The analyses were quite concordant.

From beakers in which cadmium chloride was in a large excess, there were some indications of another double salt, when the solution was evaporated nearly to dryness. Under the microscope were noticed very small rod-shaped crystals in company with the silky needles of cadmium chloride. It was found impossible to get this salt in a pure form for analysis. When water was added to the syrupy mass of mixed crystals and concentrated mother-liquors, the crystals were at once dissolved.

I. 0.1518 gram salt gave 0.2730 gram AgCl.
0.3151 gram salt gave 0.1262 gram CdO.
II. 0.0811 gram salt gave 0.1463 gram AgCl.
0.1498 gram salt gave 0.0601 gram CdO.

	Calculated for $[NH_3(CH_3)]_2CdCl_4$.	Found.	
		I.	II.
Cl	44.55	44.42	44.55
Cd	35.24	35.04	35.10

Double Bromides.

1 : 1 Methylamine Bromcadmiate.—This salt is so easily soluble that it was difficult to get it sufficiently pure for analysis. From solutions in which cadmium bromide was in the ratios 1 : 1, 2 : 1, 3 : 1, etc., to the hydrobromide of the amine, long flattened prisms with rectangular terminations were obtained. The crystals were transparent, generally very much striated, and little could be determined as to their crystal form. The very concentrated mother-liquors from which they crystallized were always colored more or less with free bromine. In order to get the salt in a pure condition, it was found necessary to get it in sufficient quantities to permit of a hasty washing. By this very wasteful process enough was obtained for analysis in two instances. Other estimations of cadmium were sufficiently close to show what the salt was.

I. 0.3040 gram salt gave 23.65 × 0.00801 Br.
0.3040 gram salt gave 0.1038 gram CdO.
II. 0.2240 gram salt gave 0.3319 gram AgBr.
0.2766 gram salt gave 0.0957 gram CdO.

	Calculated for $[NH_3(CH_3)]CdBr_3$.	Found. I.	II.
Br	62.41	62.30	62.97
Cd	29.23	29.95	29.87

2 : 1 Methylamine Bromcadmiate.—From solutions of methylamine hydrobromide and the metallic bromide mixed in the proportions 2 : 1, 3 : 1, 4 : 1, respectively, there separated from the syrupy liquid, on concentration, large tabular crystalline masses, the edges of which were fringed with dendritic forms. No well-defined individual crystals were obtained. Little trouble was experienced in getting this salt in a pure condition for analysis, and a number of concordant results were obtained.

I. 0.3593 gram salt gave 0.0932 gram CdO.
0.3552 gram salt gave 0.5394 gram AgBr.
II. 0.2860 gram salt gave 0.0746 gram CdO.
0.2249 gram salt gave 18.09 × 0.00801 Br.

	Calculated for $[NH_3(CH_3)]_2CdBr_4$.	Found. I.	II.
Cd	22.58	22.69	22.79
Br	64.51	64.54	64.42

Double Iodides.

Solutions of methylamine hydroiodide and cadmium iodide were mixed in the usual proportions and allowed to evaporate slowly.

In the beakers containing cadmium iodide in large excess, this salt crystallized out unchanged. In the other beakers, after the solutions had nearly reached dryness, a mixture of exceedingly soluble crystals was obtained. It was found impossible to effect a separation by mechanical means. The shiny hexagonal plates of cadmium iodide were easily recognized. Among these were some transparent crystalline aggregates of a different order of crystallization from the latter. Some of these were separated and dried as well as possible on filter-paper. Qualitative experiments showed the presence of considerable quantities of cadmium.

DIMETHYLAMINE SALTS.

Double Chlorides.

1 : 1 Dimethylamine Chlorcadmiate.—This salt is readily obtained from very concentrated solutions of dimethylamine hydrochloride and cadmium chloride mixed in the molecular proportions 1 : 1, 2 : 1, and 1 : 2, respectively.

The crystals obtained under different conditions differ markedly in appearance. The forms most frequently met with were long, striated, flattened prisms, obliquely terminated. Some large flattened rhombohedral prisms crystallized from a solution which was slowly evaporated for several months. Some of these were over two inches long.

Owing to the extremely concentrated solutions from which this salt comes down, the analyses in many instances were not very sharp.

However, recrystallized specimens gave results quite close to the theoretical. When heated to about 180° this salt sublimes slightly, at 240° it begins to darken, and at 261°–262° it melts quite sharply with signs of decomposition.

I. 0.5064 gram salt gave 0.2461 gram CdO.
0.2780 gram salt gave 0.4516 gram AgCl.
II. 0.1521 gram salt gave 0.0733 gram CdO.
0.2075 gram salt gave 0.3368 gram AgCl.

	Calculated for $[NH_2(CH_3)_2]CdCl_3$.	Found. I.	II.
Cd	42.36	42.52	42.16
Cl	40.17	40.12	40.09

1 : 2 Dimethylamine Chlorcadmiate.—This salt in general appearance is somewhat similar to the last-described double halide; however, its flattened, lath-shaped, transparent crystals are not so obliquely terminated. It comes down from concentrated mixtures of solutions of the two constituents in which cadmium chloride is in excess. From a mixture in the ratio 1 : 2, one crop of crystals of the 1 : 1 salt was obtained. The successive crops were the 1 : 2 salt.

The salt was drained as thoroughly as possible from mother-liquors, quickly washed with water, and pressed between folds of smooth drying-paper. As it was found to be slightly efflorescent, it was not air-dried, but weighed immediately.

The apparatus used for determining water of crystallization consisted of an air-bath through which was extended a piece of combustion tube. At either end were U-tubes containing glass beads moistened with sulphuric acid. Dried air was drawn over the salt which was placed in a porcelain boat in the tube.

A constant weight was obtained with the salt in question after heating for one hour at 110°. No further loss was noted on raising the temperature to 125°. At 170° there were signs of sublimation in the cold parts of the tube, but the loss in weight of the salt was very small. No signs of decomposition were apparent at 270°, when it was heated in a melting-point capillary tube.

I. 0.2466 gram salt gave 0.1412 gram CdO.
0.1092 gram salt gave 0.1739 gram AgCl.
0.6818 gram salt lost 0.0512 gram H_2O at 110°.
II. 0.1291 gram salt gave 0.0738 gram CdO.
0.2093 gram salt gave 0.3341 gram AgCl.
1.3653 grams salt lost 0.1026 gram H_2O at 110°.

	Calculated for		Found.	
	$[NH_2(CH_3)_2]Cd_2Cl_5.2H_2O$.	$[NH_2(CH_3)_2]Cd_2Cl_5$.	I.	II.
Cd	....	50.06	50.10	50.01
Cl	....	39.56	39.33	39.42
H_2O	7.44	....	7.50	7.52

3 : 2 Dimethylamine Chlorcadmiate.—From mixed solutions of the constituent halides made up in the proportions 2 : 1, 3 : 1, and 4 : 1, dimethylamine hydrochloride being in excess, no crystals appeared until evaporation had proceeded nearly to dryness.

The crystal forms usually met with under these circumstances were flat, transparent prisms having a rectangular cross-section, the corners of which were symmetrically truncated. The solution at this stage of concentration was syrupy in its consistency. After draining off the mother-liquors as thoroughly as possible, the crystals were washed with water. This seemed to cause a slight superficial decomposition, the transparent crystals being rendered somewhat translucent.

Inasmuch as salts of analogous composition have not been met with hitherto, it was thought at first that the presence of impurities had affected the analyses. Comparing the results obtained with the formula given below, it was found that the figures for chlorine were always fair, but some of the cadmium percentages were markedly low. The lowest result obtained was 35.36 per cent. It is not at all probable that this can be the 2 : 1 salt—Cd 32.3 per cent—for it was noted that the analyses made under the best conditions gave higher results for the metal than in the other cases. From a solution made up in the proportion 4 : 1, the amine hydrochloride being in excess, a crop of crystals which seemed to be homogeneous was obtained. These, on analysis, gave perfectly satisfactory results. The maximum and minimum results in the analysis of this double halide obtained from different sources are recorded below.

I. 0.1430 gram salt gave 0.0578 gram CdO.
0.0655 gram salt gave 0.1073 gram AgCl.
II. 0.4003 gram salt gave 0.1667 gram CdO.
0.1477 gram salt gave 0.2437 gram AgCl.

	Calculated for $[NH_2(CH_3)_2]_3Cd_2Cl_7$.	Found.	
		I.	II.
Cd	36.70	35.36	36.43
Cl	40.62	40.45	40.75

Double Bromides.

1 : 1 Dimethylamine Bromcadmiate.—When solutions of dimethylamine hydrobromide were mixed with equal, and with larger, molecular quantities of cadmium bromide, and the resulting solutions were allowed to evaporate spontaneously, in some instances crystals in the form of fine white needles appeared. Under other conditions long, thin, striated prisms were obtained. The analyses would indicate that they were the same salt, though the needles contained as much as 2 per cent more cadmium. By diluting and allowing the solution to evaporate very slowly, it was usually possible to get out the larger crystals, which, owing to their compact form, could be better freed from mother-liquors and dried. If the first crop of crystals is allowed to remain in the solution 1 : 4, and the solution is still further concentrated, thick, short, transparent, octahedral grains, seven mm. across, appear mixed with the flattened, lath-shaped crystals of the 1 : 1 type. A discussion of these will be taken up later.

From the solutions made up in the ratios 1 : 1 and 1 : 2, only the 1 : 1 double bromide was obtained.

I. 0.2603 gram salt gave 0.0857 gram CdO.
0.1124 gram salt gave 0.1602 gram AgBr.
II. 0.3768 gram salt gave 0.1225 gram CdO.

	Calculated for $[NH_2(CH_3)_2]CdBr_3$.	Found. I.	II.
Cd	28.20	28.80	28.44
Br	60.21	60.56	....

2 : 1 Dimethylamine Bromcadmiate.—In all cases where the hydrobromide of the amine was in excess, tabular crystalline masses with projecting rhombohedral prisms were obtained. The solutions were concentrated until they were of a syrupy consistency before any crystals appeared. Several crops from the different beakers were drained and dried and the whole recrystallized from water solution, acidulated with hydrobromic acid. The recrystallized specimens in all cases gave sharp results.

I. 0.2438 gram salt gave 0.0604 gram CdO.
0.1419 gram salt gave 0.2037 gram AgBr.
II. 0.3122 gram salt gave 0.0765 gram CdO.
0.1113 gram salt gave 0.1602 gram AgBr.

	Calculated for $[NH_2(CH_3)_2]_2CdBr_4$.	Found. I.	II.
Cd	21.42	21.67	21.44
Br	60.96	61.00	61.17

1 : 4 Dimethylamine Bromcadmiate.—When solutions in which the hydrobromide of the base bears the ratios 1 : 4, 1 : 5, etc., to the cadmium bromide, were allowed to evaporate spontaneously, there first appeared a crop of long striated, prismatic crystals, which proved on analysis to be the 1 : 1 double bromide. If, without removing these, the solution was still further concentrated, under the crystalline crust, formed as the solution approaches dryness, short, thick, brilliant crystals appeared. These were hard and compact and could be washed by picking them out one by one on a platinum spatula and dipping them momentarily in a beaker of water. When water was added to the mixture of crystals mentioned above, all quickly dissolved except the short, thick grains. The latter became somewhat opaque, owing to a slight surface decomposition. The analyses were not all concordant, but were fair considering the conditions under which the salt was obtained. The lowest result for cadmium recorded below is from an analysis of a recrystallized specimen of the salt.

I. 0.2458 gram salt gave 0.1051 gram CdO.
0.1640 gram salt gave 0.2279 gram AgBr.
II. 0.2296 gram salt gave 0.0955 gram CdO.

	Calculated for $[NH_2(CH_3)_2]Cd_4Br_9$.	Found.	
		I.	II.
Cd	36.98	37.41	36.39
Br	59.21	59.05	....

Double Iodides.

1 : 1 Dimethylamine Iodocadmiate.—From solutions containing dimethylamine hydroiodide and cadmium iodide in the ratios 1 : 1 and 1 : 2, respectively, tabular, cubical, crystalline masses appeared when the solution had become quite concentrated. The crystals were lifted out, dipped in water, and quickly dried between folds of filter-paper.

When cadmium iodide was in large excess it crystallized out unchanged from the mixed solutions. In the beakers containing the hydroiodide of the amine in excess, crystals appeared only after the solutions had reached a somewhat viscous state. It was found impossible to get them out in a condition approximating purity, so no analyses were made. Alcohol was then tried as a solvent, but with no better results.

0.2938 gram salt gave 0.0703 gram CdO, and 0.3828 gram AgI.

	Calculated for $[NH_2(CH_3)_2]CdI_3$.	Found.
Cd	20.84	20.93
I	70.60	70.35

TRIMETHYLAMINE SALTS.

Double Chlorides.

1 : 1 Trimethylamine Chlorcadmiate.—This salt has already been described and its crystallographic properties investigated by Hiortdahl.[1] It crystallizes from all the mixtures tried, 4 : 1 to 1 : 4, inclusive. When the solutions of the two constituents are rather concentrated, on mixing, the double halide comes down as a white crystalline precipitate. This is sparingly soluble in cold water, easily soluble in warm. From the solution, on standing, beautiful, transparent, monoclinic prisms, several mm. across, appear. These often assume a pseudohexagonal form. Twinning is also quite frequent. The salt crystallizes unchanged from water solution. There were no signs of decomposition when the salt was heated to 270°.

I. 0.4146 gram salt gave 0.1903 gram CdO.
0.3861 gram salt gave 0.5951 gram AgCl.
II. 0.4285 gram salt gave 0.1968 gram CdO.
0.4818 gram salt gave 0.8711 gram AgCl.

	Calculated for $[NH(CH_3)_3]CdCl_3$.	Found. I.	II.
Cd	40.23	40.16	40.18
Cl	38.15	38.07	38.01

3 : 2 Trimethylamine Chlorcadmiate.—After one crop of crystals of the 1 : 1 double chloride above described had been obtained from the solution made up in the ratio 4 : 1 (amine in excess), there appeared, on further concentration, obliquely terminated, flattened prisms. Inasmuch as the formula to which the analyses agreed is an unusual one, it was thought that possibly it might be the 2 : 1 salt, and that the discrepancy in cadmium might arise from impurities. The work was repeated several times, and there seems to be little doubt that the formula below correctly represents the compound. Enough was obtained to admit of a hasty washing with water.

The analyses made, under the most favorable conditions, give a higher percentage for cadmium than in the other cases.

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[1] Ztschr. für Kryst., 6, 466; Jahr., 1882, 475.

This would indicate that the impurities tend to lower the percentage of cadmium in the compound, which argues against its being the 2 : 1 salt.

I. 0.1111 gram salt gave 0.0429 gram CdO.
0.1338 gram salt gave 0.2053 gram AgCl.
II. 0.0693 gram salt gave 0.0268 gram CdO.
0.0693 gram salt gave 0.1066 gram AgCl.

	Calculated for $[NH(CH_3)_3]_3Cd_2Cl_7$.	Found. I.	II.
Cd	34.34	33.78	33.88
Cl	37.99	37.90	37.99

Double Bromides.

1 : 1 Trimethylamine Bromcadmiate.—Hiortdahl[1] has described the crystallographic properties of this salt in an article previously referred to. When a mixture of solutions of trimethylamine hydrobromide and cadmium bromide in which the latter is in excess, is concentrated to such an extent that crystals are formed on cooling, a network of long, thin, prismatic crystals separate. These are apparently homogeneous, but no concordant results can be obtained when the crystals are in this form. It is probable that the high percentage for cadmium is to be explained by the fact that the crystals in this form presented a large surface, which prevented the perfect separation of the mother-liquors rich in cadmium bromide. From these same solutions, on slow evaporation, short, thick, skeleton crystals, apparently pseudohexagonal in form, were obtained. The analyses of these were satisfactory in all cases.

I. 0.2627 gram salt gave 0.0819 gram CdO.
0.2071 gram salt gave 0.2825 gram AgBr.
II. 0.1550 gram salt gave 0.0482 gram CdO.

	Calculated for $[NH(CH_3)_3]CdBr_3$.	Found. I.	II.
Cd	27.24	27.27	27.14
Br	58.16	57.97	....

3 : 2 Trimethylamine Bromcadmiate.—When the hydrobromide of the amine was in excess in mixed solutions of cadmium bromide and the former, the above double bromide was obtained. The first crops of crystals on analysis gave high results for cadmium, but the successive crops agreed closely with the assigned formula.

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[1] Ztschr. für Kryst., 6, 467; Jahr., 1882, 475.

The form of the crystals varied widely with the conditions under which they were obtained. Those giving the most concordant results were narrow, flattened, transparent prisms, terminating in pyramidal planes.

The first crops of long, white, striated prisms which gave high results for cadmium, on recrystallization gave fair results. In all cases, when recrystallization was resorted to, the percentage of cadmium was lowered.

I. 0.2680 gram salt gave 0.0716 gram CdO.
II. 0.2384 gram salt gave 0.0639 gram CdO.
0.1243 gram salt gave 0.1702 gram AgBr.
0.5039 gram salt gave 11.56 × 8.104 mgms. $N(CH_3)_3$.

	Calculated for $[NH(CH_3)_3]_3Cd_2Br_7$.	Found. I.	Found. II.
Cd	23.28	23.32	23.45
Br	58.00	58.17	....
$N(CH_3)_3$	18.40	18.58	....

Double Iodides.

1 : 1 Trimethylamine Iodocadmiate.—This salt crystallizes in splendid large cubical masses, resembling potassium iodide in general appearance. From some of the beakers only individual transparent cubes were obtained. These presented a remarkable play of colors in the sunlight. The solutions from which this salt crystallized were made up in the ratios 1 : 1, 1 : 2, 1 : 3, etc.; *i. e.*, cadmium iodide in equal and in larger molecular quantities.

I. 0.2055 gram salt gave 0.0480 gram CdO.
II. 0.4505 gram salt gave 0.1028 gram CdO.
0.1141 gram salt gave 0.1458 gram AgI.

	Calculated for $[NH(CH_3)_3]CdI_3$.	Found. I.	Found. II.
Cd	20.30	20.43	19.97
I	68.81	....	69.00

2 : 1 Trimethylamine Iodocadmiate.—When the molecular ratios of the two halides, trimethylamine hydroiodide and cadmium iodide, stand to each other 2 : 1, 3 : 1, etc., in solution, and the mixture is allowed to evaporate slowly, very beautiful transparent crystals appear. These are usually modified rhombic prisms. The crystals separated out as individuals in every case. In some instances the 1 : 1 and 2 : 1 double iodides crystallized out side by side in the same beaker. But the difference in crystal form made it easy to effect a separation by mechanical means.

Both of the latter salts are much less soluble in water than the above-described trimethylamine double bromides.

I. 0.3689 gram salt gave 0.0643 gram CdO.
II. 0.3022 gram salt gave 0.0524 gram CdO.
0.1140 gram salt gave 0.1451 gram AgI.

	Calculated for $[NH(CH_3)_3]_2CdI_4$.	Found.	
		I.	II.
Cd	15.17	15.25	15.13
I	68.56	68.72	....

TETRAMETHYLAMMONIUM SALTS.

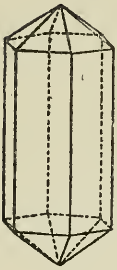
Double Chlorides.

1 : 1 Tetramethylammonium Chlorcadmiate.—This double salt crystallized in magnificent hexagonal prisms several cm. long. It was obtained from every mixture of the constituent halides experimented with. When the mixed solutions were concentrated to such an extent that crystals were formed on cooling, the results obtained on analysis were not sharp. The slender white columnar crystals formed under such circumstances seemed to hold the mother-liquors with great persistence. On recrystallization the percentage for cadmium accorded with the assigned formula below. The double salt in the form of the hexagonal prisms above mentioned always gave sharp results. This compound crystallized from water unchanged.

Inasmuch as there are double bromides and double iodides formed in the ratio 2 : 1, it was thought that an analogue might be obtained in this series; but there was no evidence of a salt of this composition. From a solution containing mixtures of the two chlorides in the proportion 4 : 1, the ammonium salt in excess, four successive crops of the 1 : 1 compound were obtained before evaporation had proceeded to such an extent that nothing definite could be further isolated from the mother-liquor.

I. 0.4074 gram salt gave 0.1780 gram CdO.
0.1613 gram salt gave 0.2361 gram AgCl.
II. 0.2054 gram salt gave 0.0893 gram CdO.

	Calculated for $[N(CH_3)_4]CdCl_3$.	Found. I.	II.
Cd	38.29	38.23	38.04
Cl	36.32	36.15	....



Crystallography.[1]

Hexagonal.

P : P = 142° 15′
P : ∞P = 130° 21′
∞P : ∞P = 120°
Axis c′ = 0.734872

Double Bromides.

1 : 1 Tetramethylammonium Bromcadmiate.—When concentrated water solutions of cadmium bromide and tetramethylammonium bromide were mixed in the cold in any of the ratios 4 : 1 – 1 : 4, inclusive, a white crystalline precipitate was formed. The precipitates thus formed were redissolved and the solutions diluted. On slow evaporation large, transparent, hexagonal prisms terminating in pyramidal faces were obtained. These very much resemble the double chloride last described. This salt was readily obtained quite pure. The analyses in all instances were consistent with each other and corresponded to the calculated value below.

I. 0.3637 gram salt gave 0.1094 gram CdO.
0.2452 gram salt gave 0.3240 gram AgBr.
II. 0.1822 gram salt gave 0.0547 gram CdO.

	Calculated for $[N(CH_3)_4]CdBr_3$.	Found. I.	II.
Cd	26.34	26.31	26.26
Br	56.24	56.15	....

2 : 1 Tetramethylammonium Bromcadmiate.—From mixed solutions of the two bromides in which tetramethylammonium bromide was in excess several crops of the 1 : 1 double bromide were first obtained, but finally short, inperfect, flattened rhombic prisms appeared after the solutions had been further concentrated. Mechanical separation had to be used in some cases.

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[1] I am indebted to Dr. F. P. King, of the Department of Mineralogy, for the crystallographic work. I would take this occasion to express my thanks.

When the crystals were homogeneous, the analyses were always close for the formula assigned.

I. 0.2777 gram salt gave 0.0612 gram CdO.
0.1822 gram salt gave 0.2359 gram AgBr.
II. 0.1575 gram salt gave 0.0349 gram CdO.

	Calculated for $[N(CH_3)_4]_2CdBr_4$.	Found. I.	II.
Cd	19.35	19.28	19.38
Br	55.08	55.02	....

Double Iodides.

1 : 1 Tetramethylammonium Iodocadmiate.—Like the analogous double bromide of tetramethylammonium, this salt is sparingly soluble in cold water. From dilute solutions of the two iodides, in which cadmium iodide was in excess, a white coating of individual crystalline grains appeared on the sides and the bottom of the beakers containing the mixture. The crystal form of the grains, some of which were of microscopic size, was rather indefinite. The mother-liquor, poured off the crystals, deposited, on standing a short time, another crop of the same crystals.

In some of the succeeding crops of crystals, the characteristic double iodide 2 : 1 described below was noticed.

No evidence of a double salt having a higher proportion of cadmium iodide was obtained. From a solution containing 0.625 gram of tetramethylammonium iodide and 15 grams of cadmium iodide only the 1 : 1 double iodide came down on slow evaporation.

I. 0.2981 gram salt gave 0.0665 gram CdO.
0.1786 gram salt gave 0.2213 gram AgI.
II. 0.2467 gram salt gave 0.0559 gram CdO.

	Calculated for $[N(CH_3)_4]CdI_3$.	Found. I.	II.
Cd	19.80	19.51	19.82
I	67.10	66.91	....

2 : 1 Tetramethylammonium Iodocadmiate.—The crystals of this salt usually appeared as white, feathery, individual crystals terminating in a very acute angle. These covered the walls and the bottom of the beaker as a crystalline coating. When the first crop had separated out and the mother-liquor had been allowed to evaporate spontaneously, tabular, transparent crystals, several mm. broad, were formed. These were imperfect, but their general outline seemed to indicate that they were modified tetrahedra. Both this salt and the one last described were very brilliant, and exhibited a remarkable play of colors in the sunlight. The beakers from which the compound was obtained contained an excess of tetramethylammonium iodide. In some cases the two double halides, 1 : 1 and 2 : 1, were noticed in the same beaker. The crystals were too small to be separated conveniently by mechanical means, but the crystal forms were easily recognizable.

I. 0.4543 gram salt gave 0.0762 gram CdO.
0.3559 gram salt gave 0.4348 gram AgI.
II. 0.2866 gram salt gave 0.0476 gram CdO.

	Calculated for $[N(CH_3)_4]_2CdI_4$.	Found. I.	II.
Cd	14.62	14.67	14.53
I	66.05	65.94	....

Conclusions.

1. All the double halides of the alkali metals and ammonium with cadmium, described in the literature, may be classified under the types 1 : 1, 2 : 1, 3 : 1, 4 : 1.

Among the double halides described in this paper, the types met with are 1 : 2, 2 : 1, 3 : 2, 1 : 2, 1 : 4.

Of these it will be noted that the last three types have no analogues among the double halides of the alkali metals and ammonium with cadmium.

2. No double halides corresponding to $(NH_4)_4CdCl_6$ and $(NH_4)_4CdBr_6$., *i. e.* the 4 : 1 type, were obtained.

3. Of the 21 compounds described in this paper, 18 conform to Remsen's law. Three fall under the extension of the law.

SOME DOUBLE HALIDES OF TIN WITH THE ALIPHATIC AMINES AND WITH TETRAMETHYLAMMONIUM.[1]

BY C. G. COOK.

The work of Slagle,[2] on the double halides of tin with substituted ammonia compounds, has been extended in this investigation to the compounds formed with the aliphatic amines and with tetramethylammonium.

Preparation of Material.

Amines.—The bases were obtained from the salts furnished by Bender and Hobein.

Tetramethylammonium hydroxide was prepared from its salts by treatment with moist silver oxide according to Hofmann's method[3] and the required salt obtained by neutralizing with the corresponding acid.

Stannous chloride and bromide were made by dissolving the metal in hydrochloric and hydrobromic acids.

The stannic chloride used had been previously prepared by passing chlorine over tin, and was purified by distillation from tin.

Stannic bromide was obtained by the action of bromine on tin. The bromine was allowed to fall, drop by drop, on granulated tin contained in a retort. The reaction, which required but a gentle heat for its initiation, was very violent and continued so long as bromine was added. The product mixed with excess of bromine, distilled over into the receiver and after being purified by fractional distillation was a liquid of light-yellow color which, on cooling, solidified in beautiful white crystals.

Methods of Analysis.

Tin in chlorstannites was determined by dissolving in a solution of ferric chloride in hydrochloric acid, heating to boiling, diluting with water, cooling, and titrating the ferrous chloride (formed by the reduction of the ferric chloride) with a standard solution of potassium permanganate.

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[1] From the author's dissertation, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1898. The work was undertaken at the suggestion of Professor Remsen and carried out under his guidance.

[2] This JOURNAL, 20, 633.

[3] J. Chem. Soc., 4, 307.

Stannic tin was determined by reducing to the metallic state with zinc and hydrochloric acid and treating the reduced metal as above. In a few cases tin was estimated as the oxide by evaporating the salt in a weighed crucible with nitric acid and incinerating the base according to the method of Carnelly and O'Shea[1] for determination of tin in stannic bromide, but the method was not found satisfactory.

Amines were estimated by decomposing the salts with sodium or potassium hydroxide and distilling with the aid of steam. The distillate was collected in a known quantity of standard acid and the excess of acid titrated with standard potassium hydroxide solution. For the distillation, a gang-still, composed of four block-tin coils cooled in a water-tank, was used. The method was found both exact and rapid.

The tin of bromstannites was determined by reduction as in the case of stannic salts, since the hydrobromic acid prevented the use of the method applied to chlorstannites.

Preparation of Double Salts.

Concentrated solutions of the two salts were mixed in small beakers in various molecular proportions, as 1 : 1, 1 : 2, 3 : 2, 4 : 1, etc. The mixtures, after being acidulated with the corresponding acids, were evaporated, either by heating or in sulphuric acid and caustic soda desiccators. The successive homogeneous crops of crystals were dried, by pressing between folds of drying-paper, and analyzed.

Compounds Described.

1 : 1 Methylamine chlorstannite.
2 : 1 Methylamine chlorstannate.
1 : 1 Dimethylamine chlorstannite.
2 : 1 Dimethylamine chlorstannate.
1 : 1 Trimethylamine chlorstannite.
2 : 1 Trimethylamine chlorstannate.
1 : 1 Tetramethylammonium chlorstannite.
2 : 1 Tetramethylammonium chlorstannate.

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[1] J. Chem. Soc., 33, 55.

1 : 1 Ethylamine chlorstannite.
2 : 1 Ethylamine chlorstannate.
1 : 1 Triethylamine chlorstannate.
2 : 1 Triethylamine chlorstannate.
3 : 1 Triethylamine chlorstannate.
1 : 1 Methylamine bromstannite.
2 : 1 Methylamine bromstannate.
1 : 1 Dimethylamine bromstannite.
2 : 1 Dimethylamine bromstannate.
2 : 1 Trimethylamine bromstannate.
1 : 1 Ethylamine bromstannite.
2 : 1 Ethylamine bromstannate.
2 : 1 Triethylamine bromstannate.

DOUBLE CHLORIDES.

Methylamine Salts.

1 : 1 Methylamine Chlorstannite, $CH_3NH_3SnCl_3$.—This salt was obtained from a number of mixtures of methylamine hydrochloride and stannous chloride. The crystals were well-defined, transparent, and prismatic in form. Their crystallographic measurements, however, were not made. The salt was much less soluble than stannous chloride, as was shown by the fact that in a few cases the excess of stannous chloride crystallized out in nearly pure condition. Analysis :

	Calculated for $CH_3NH_3SnCl_3$.	Found. I.	II.	III.
NH_3CH_3	12.52	12.51	....	12.48
Sn	46.01	45.98	45.99	....

2 : 1 Methylamine Chlorstannate, $[CH_3NH_3]_2SnCl_6$.—Several mixtures of methylamine hydrochloride and stannous chloride became oxidized by the air, and crystals were formed which proved, on analysis, to be 2 : 1 methylamine chlorstannate. This salt had been described by Hiortdahl.[1] In one case a small crop of white pellets mixed with other crystals was formed. These were separated mechanically, and as a determination of the base seemed to indicate a 1 : 1 stannic salt, an extensive investigation was undertaken to obtain this salt in sufficient quantity for complete anlaysis.

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[1] Ztschr. für Kryst., **6**, 462.

For this purpose a series of mixtures of methylamine hydrochloride and stannic chloride were made, and the successive crops of crystals analyzed, but all analyses indicated the 2 : 1 salt only. The crystals seemed to be of two forms: the one form, hexagonal rhombohedral, as described by Hiortdahl, the other, transparent scales.

	Calculated for $[CH_3NH_3]_2SnCl_6$.	Found. I.	II.	III.
CH_3NH_3	16.23	16.20	16.25	....
Sn	29.86	30.03	....	30.16

Dimethylamine Salts.

1 : 1 Dimethylamine Chlorstannite, $(CH_3)_2NH_2SnCl_3$.—When concentrated solutions of dimethylamine hydrochloride and stannous chloride were mixed, this salt formed in needle-like crystals. In some cases the crystals seemed to be rhombic, but none could be obtained suitable for crystallographic work. In two beakers the excess of stannous chloride crystallized out in nearly pure condition, showing the difference in solubility of the two salts.

	Calculated for $(CH_3)_2NH_2SnCl_3$.	Found. I.	II.	III.
$(CH_3)_2NH_2$	17.04	17.11	....	17.06
Sn	43.61	....	43.64	43.65

2 : 1 Dimethylamine Chlorstannate, $[(CH_3)_2NH_2]_2SnCl_6$.—A number of mixtures of dimethylamine hydrochloride and stannous chloride, made for the purpose of obtaining chlorstannites, became oxidized. In these, crops of transparent crystals formed. These, on analysis, proved to be the 2 : 1 dimethylamine salt described by Hiortdahl.[1]

Further work showed that this salt crystallized from all mixtures of dimethylamine hydrochloride and stannic chloride on concentration. The salt formed four-sided tables generally. Analysis:

	Calculated for $[(CH_3)_2NH_2]_2SnCl_6$.	Found. I.	II.	III.	IV.
$(CH_3)_2NH_2$	21.79	21.7	21.8	....	....
Sn	27.88	...	...	27.81	27.71

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[1] Ztschr. für Kryst., 6, 464.

Trimethylamine Salts.

1 : 1 Trimethylamine Chlorstannite, $(CH_3)_3NHSnCl_3$.—This salt is difficultly soluble and comes down almost quantitatively as a white precipitate from mixtures of concentrated solutions of its constituents. From more dilute solutions, however, crystals in the form of triangular plates were formed. No specimens were obtained suitable for crystallographic work. A large number of determinations of base and tin were made, many of which indicated the 1 : 1 salt.

	Calculated for $(CH_3)_3NHSnCl_3$.	Found.			
		I.	II.	III.	IV.
$(CH_3)_3NH$	21.13	21.07	....	21.09	....
Sn	41.46	....	41.57	....	41.58

2 : 1 Trimethylamine Chlorstannate, $[(CH_3)_3NH]_2SnCl_6$.—This salt was obtained from a number of mixtures of trimethylamine hydrochloride and stannous chloride which were oxidized by the air. The salt had been previously made by Hiortdahl.[1] The crystals were well formed and often of quite good size. Their form is a combination of the cube and octahedron.

	Calculated for $[(CH_3)_3NH]_3SnCl_6$.	Found.		
		I.	II.	III.
$(CH_3)_3NH$	26.66	26.51	....	26.81
Sn	26.15	....	25.72	....

Tetramethylammonium Salts.

1 : 1 Tetramethylammonium Chlorstannite, $(CH_3)_4NSnCl_3$.—This salt is formed in all mixtures of the chloride of the base with stannous chloride. The salt was precipitated from moderately concentrated solutions in the form of a crystalline powder, which was dried with difficulty by pressing between folds of drying-paper. In more dilute solutions the crystals took the form of needles. Those solutions which contained an excess of the chloride of the base were easily oxidized during evaporation.

	Calculated for $N(CH_3)_4SnCl_3$.	Found.	
		I.	II.
Sn	39.51	39.59	39.37

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[1] Ztschr. für Kryst., 6, 466.

2 : 1 Tetramethylammonium Chlorstannate, $[N(CH_3)_4]_2SnCl_6$.—When moderately concentrated solutions of stannic chloride and tetramethylammonium chloride were mixed in any proportion a salt was formed which was shown by analysis to have the above formula. The crystals were generally small and not easily soluble in hot, dilute hydrochloric acid. From this solution the salt recrystallized, on cooling, in beautiful, brilliant crystals, which were a combination of the cube and octahedron. Analysis:

	Calculated for $[N(CH_3)_4]_2SnCl_6$.	Found.		
		I.	II.	III.
Sn	24.62	24.3	24.35	....
Cl	44.43	...	....	44.21

Specimens suitable for crystallographic measurements were obtained and the results will be given in a future publication.

Ethylamine Salts.

1 : 1 Ethylamine Chlorstannite, $NH_3C_2H_6SnCl_3$.—This salt was easily formed when concentrated solutions of the hydrochloride of the base and stannous chloride were mixed in various proportions. If the solutions were not too concentrated, the salt formed in white needles soluble in dilute acid. Quite dilute solutions generally became oxidized during evaporation and gave crops of crystals mixed with a stannic salt or composed entirely of the stannic salt. No specimens could be obtained suitable for crystallographic work. Analysis showed the salt to be isomeric with the 1 : 1 dimethylamine chlorstannite.

	Calculated for $C_2H_5NH_3SnCl_3$.	Found.		
		I.	II.	III.
$C_2H_5NH_3$	17.04	17.09	16.99	....
Sn	43.61	43.52	....	43.61

2 : 1 Ethylamine Chlorstannate, $[C_2H_5NH_3]_2SnCl_6$.—The crystals obtained from the oxidized solutions of ethylamine hydrochloride and stannous chloride, mentioned above, as well as from a number of mixtures of stannic chloride and the hydrochloride of the base in various proportions, were found, on analysis, to be the same salt—the 2 : 1 ethylamine chlorstannate. This is isomeric with the 2 : 1 dimethylamine chlorstannate and, like it, crystallizes well. The crystals are made up of combinations of pyramidal and prismatic faces, in some cases the prismatic form occurring to the exclusion of the pyramids, while in others the latter predominate, giving the crystals an entirely different appearance. The crystals are tough, translucent, and with but little luster.

	Calculated for	Found.			
	$[C_2H_5NH_3]_2SnCl_6$.	I.		II.	III.
$C_2H_5NH_2$	21.79	....		21.82	21.75
Sn	27.88	27.58	27.52	....	....

Triethylamine Salts.

When triethylamine hydrochloride and stannous chloride were mixed in concentrated solution there was no evidence of the formation of a double salt, and all attempts to concentrate the solution sufficiently for crystallization to take place only led to the oxidation of the tin salt, and the formation of chlorstannates. To prevent this oxidation, an attempt was made to keep the beakers containing the solutions in an atmosphere of carbon dioxide for some weeks, but evaporation was so slow that sufficient oxygen from the air found its way into the solutions to produce oxidation, and chlorstannates were again formed. The crystals formed by the oxidation of all the above-mentioned mixtures, as well as those from mixtures of triethylamine hydrochloride and stannic chloride were, in general, in the form of rhombic plates, joined by their corners into masses. In some cases the individual crystals showed a tendency to curl up, giving the cluster something of the appearance of a rose. A few large, well-formed crystals were obtained, which much resembled Iceland spar.

About 24 determinations of base were made in the various specimens of crystals, with the most discordant results, and crystals of apparently the same form proved, on analysis, to be mixtures of salts with from 1 to 3 molecules of base. In a few samples which proved to be nearly pure 2 : 1 triethylamine chlorstannate the tin and base were determined with reasonably good results, as follows:

	Calculated for $[(C_2H_5)_3NH]_2SnCl_6$.	Found. I.	II.	III.
$(C_2H_5)_3NH$	38.20	38.20	38.35	37.78
Sn	22.03	21.96	....	22.07

In a number of cases the figures for the base were in the neighborhood of those required by the 1 : 1 salt:

	Calculated for $(C_2H_5)_3NHSnCl_5$.	Found. I.	II.	III.
$(C_2H_5)_3NH$	25.71	26.94	26.17	26.19

Quite a number of the base determinations ran above the per cent required for the 2 : 1 salt, and a few approached the value of the 3 : 1 salt:

	Calculated for $[(C_2H_5)_3NH]_3SnCl_7$.	Found. I.	II.
Base	45.57	44.75	43.85

In almost all cases the crystals had the appearance of those of a pure salt, and in nearly all cases analysis showed them to be mixtures.

DOUBLE BROMIDES.

The preparation of the bromstannites was found to be accompanied with much more difficulty than that of the corresponding chlorine salts. Not only did the solutions oxidize so easily on standing that successive crops of crystals could not be obtained, but also the crystals when removed from the mother-liquor were dried with more difficulty, and in a few cases became oxidized after they had been dried by being pressed between numerous folds of drying-paper. For these and other reasons, the preparation of a few of the possible salts was abandoned. The crystals were generally small and of forms difficult to determine.

The bromstannates, on the other hand, are generally beautifully crystallized, and a number of specimens suitable for crystallographic work were obtained.

Methylamine Salts.

1 : 1 Methylamine Bromstannite, $CH_3NH_3SnBr_3$.—When quite concentrated solutions of methylamine hydrobromide and stannous bromide were mixed the solution remained clear for a moment and then a bright red precipitate was formed in large quantity. This precipitate dissolved to a colorless, or nearly colorless, solution on the addition of water. From more dilute solutions the salt made its appearance in the form of dark-red, shining scales.

A dilute solution was concentrated by heating, and, on cooling, red needles appeared, arranged in the form of cubes with beautifully fringed edges. These crystals, after standing some days in the mother-liquor, were subjected to the method for determining bases and found to contain a considerable quantity of a bromstannate. Other crystals, which were allowed to stand under similar circumstances, disappeared and a yellow bromstannate took their place. Crystals which were carefully dried soon after precipitation were analyzed and the following results obtained :

	Calculated for $CH_3NH_3SnBr_3$.	Found.			
		I.	II.	III.	IV.
CH_3NH_3	8.22	8.28	....	8.27	....
Sn	30.25	...	30.36	...	29.95

2 : 1 Methylamine Bromstannate, $[CH_3NH_3]_2SnBr_6$.—The crystals of this salt were generally small and not well defined. They formed slowly when mixtures of their constituents were allowed to evaporate spontaneously. Their shape and appearance were quite variable, but analysis showed them to be generally nearly pure. The most common form was that of yellow pellets composed of gummy crystal masses. In a number of cases yellow hexagonal plates were noticed. At other times the salt formed as scales, a few of which were so thin as to appear iridescent.

Among the analyses were the following :

	Calculated for $[CH_3NH_3]_2SnBr_6$.	Found.			
		I.	II.	III.	IV.
CH_3NH_3	9.69	9.63	....	9.70	....
Sn	17.82	...	18.00	...	18.20

Dimethylamine Salts.

1 : 1 Dimethylamine Bromstannite, $(CH_3)_2NH_2SnBr_3$.—This salt was made from a number of mixtures of dimethylamine hydrobromide and stannous bromide, as a crystalline precipitate in the form of beautiful, brilliant, white scales or feathers. Several times it came down with a light-yellow or brown tint, probably due to impurity in the form of a bromstannate.

	Calculated for $(CH_3)_2NH_2SnBr_3$.	Found.		
		I.	II.	III.
$(CH_3)_2NH_2$	11.41	11.21	11.21	....
Sn	29.20	....	....	28.93

2 : 1 Dimethylamine Bromstannate, $[(CH_2)_2NH_2]_2SnBr_6$.—This salt was made in the usual way by mixing its constituents in a number of proportions and allowing the mixtures to evaporate spontaneously. The crystals, which formed readily and in good size, were brilliant, transparent, hexagonal prisms with modified ends. Analysis :

	Calculated for $[(CH_3)_2NH_2]_2SnBr_6$.	Found.		
		I	II.	III.
$(CH_3)_2NH_2$	13.11	13.14	....	13.14
Sn	17.14	16.76	16.94	....

Trimethylamine Salts.

The hydrobromide of the base was mixed with stannous bromide in a number of proportions, and one crop of white, feather-like crystals and needles was obtained from one beaker, but the solutions showed such a tendency to become oxidized that further efforts to obtain the salt were abandoned.

2 : 1 Trimethylamine Bromstannate, $[(CH_3)_3NH]_2SnBr_6$.—The crystals of this salt were generally small, but under the glass seemed to resemble those of trimethylamine chlorstannate and were probably a combination of cube and octahedron. They were nearly transparent and of a yellow color. Analysis :

	Calculated for $[(CH_3)_3NH]_2SnBr_6$.	Found.		
		I.	II.	III.
$(CH_3)_3NH$	16.75	16.39	....	....
Sn	16.43	....	16.59	16.67

Ethylamine Salts.

1 : 1 Ethylamine Bromstannite, $C_2H_5NH_3SnBr_3$.—Owing to the ease with which the solutions of this salt became oxidized, a large number of crops of the crystals were not obtained, but analysis clearly established their composition to be isomeric with the 1 : 1 dimethylamine bromstannite mentioned above.

The crystals were yellowish-white, shining, semi-transparent, and needle-like in form.

	Calculated for	Found.			
	$C_2H_5NH_3SnBr_3$.	I.		II.	
$C_2H_5NH_3$	11.41	....	....	11.48	11.48
Sn	29.2	29.05	29.46	....	....

2 : 1 Ethylamine Bromstannate, $[C_2H_5NH_3]_2SnBr_6$.—The forms of the crystals of this salt were much like those of the corresponding chlorine salt, but in other characteristics the crystals showed more resemblance to the isomeric 2 : 1 dimethylamine bromstannate. They were lustrous, of a bright-yellow color, and nearly transparent. In most cases the prismatic faces, and also the pyramidal ones, were developed, but some crystals on which the pyramidal form predominated were noticed.

	Calculated for		Found.	
	$[C_2H_5NH_3]_2SnBr_6$.	I.	II.	III.
$C_2H_5NH_3$	13.11	13.26	....	13.37
Sn	17.14	....	17.15	....

Triethylamine Salts.

When triethylamine hydrobromide was mixed with stannous bromide, beautiful, white, lustrous fibers were formed. The crystals were removed from several beakers and dried with difficulty by pressing between folds of drying-paper. After these crystals were dry, or nearly so, they became bright-yellow. This was supposed to be due to oxidation, and further work with this salt was abandoned.

2 : 1 Triethylamine Bromstannate, $[(C_2H_5)_3NH_2]_2SnBr_6$.—This salt was obtained in the usual manner, but no specimens of crystals suitable for measurement were obtained. In general, the form was that of rhombic plates, somewhat resembling those of the corresponding chlorine salt; they were yellow in color, and in some cases transparent. The percentage of base was in a number of analyses a little high, but there was no evidence of the formation of other salts as in the case of the triethylamine chlorine salts. Analysis:

	Calculated for		Found.	
	$[(C_2H_5)_3NH]_2SnBr_6$.	I.	II.	
$(C_2H_5)_3NH$	25.49	....	25.53	25.53
Sn	14.70	14.77	....	....

Conclusions.

A marked regularity is found throughout this whole series of salts. All of them, with one exception, belong to the 1 : 1 or 2 : 1 form, and all obey Remsen's law as first stated. The chlorine and bromine salts show many crystallographic resemblances, though their colors are often different.

The salts containing tin in the stannous condition seem to show differences in the ease with which they are oxidized, but so many modifying influences come in that no generalizations can be made.

NOTES ON THE DOUBLE HALIDES OF TIN WITH THE ORGANIC BASES.

By George M. Richardson and Maxwell Adams.

Practically all of our work upon the double chlorides of tin with aniline and the toluidines has been anticipated by the work of Slagle,[1] and was discontinued upon learning of his work upon these compounds.

Although our work, for the most part, confirms the results given by Slagle, we have, however, obtained some compounds not described by him, and it seems that a brief description of these may not be out of place.

Aniline Compound.

Tetraniline Chlorstannate, $(C_6H_5NH_3)_4SnCl_8$.—This compound was obtained by mixing 300 cc. of a normal aniline hydrochloride solution with 50 cc. of a normal stannous chloride solution. This mixture, on standing three days, gave a considerable yield of the dianiline chlorostannite,

$$(C_6H_5NH_3)_2SnCl_4,$$

but the mother-liquor from these crystals, after standing three weeks, gave a crop of clear, well-formed crystals, which gave upon analysis :

	Calculated for $(C_6H_6NH_3)_4SnCl_8$.	Found. A.	B.
Sn	15.16	14.91	14.98
Cl	36.50	36.48	36.37

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[1] This Journal, **20**, 633.

The mother-liquor from these crystals after standing two months more, gave still another crop of crystals, evidently like the previous ones, which gave on analysis :

	Found.	
	A.	B.
Sn	14.97	14.94
Cl	36.18	36.13

These crystals are well formed and the salt is comparatively stable.

Dimethylaniline Salts.

Working with dimethylaniline we have obtained only the dimethylaniline chlorostannite.

Dimethylaniline Chlorostannite, $C_6H_5NH(CH_3)_2SnCl_3.\frac{1}{2}H_2O$. —While this salt was evidently the one most readily formed, we have no reason to believe that others could not be obtained. This compound was, in its preparation and crystalline form, strictly analogous to the corresponding toluidine compounds described by Slagle.[1]

The salt gave upon analysis :

	Calculated for $C_6H_5NH(CH_3)_2SnCl_3.\frac{1}{2}H_2O$.	Found. A.	B.
Sn	33.19	33.09	33.13
Cl	29.96	30.40	30.49
H_2O	2.53	2.65	....

Double Bromides of Aniline and Tin.

Three distinct salts of aniline hydrobromide and tin bromide have been prepared and analyzed ; they are :

Aniline bromostannite, $C_6H_5NH_3SnBr_3$,
Dianiline bromostannate, $(C_6H_5NH_3)_2SnBr_6$, and
Tetraniline bromostannate, $(C_6H_5NH_3)_4SnBr_8$.

Aniline Bromostannite, $C_6H_5NH_3SnBr_3$.—This salt was prepared by mixing hot solutions of aniline hydrobromide and stannous bromide in molecular proportions, and allowing the mixture to stand for six or twelve hours.

The crystals were small but well defined, with a spear-like form, being white at first but changing to a yellow color upon standing. The crystals melted at 152° and were soluble in water, the solution rapidly becoming turbid. They were also soluble in alcohol, ether, and chloroform, but any attempt to recrystallize the salt from these solvents resulted in the oxidation of the tin to the stannic condition.

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[1] This JOURNAL, **20**, 640.

Analysis of this salt gave :

	Calculated for $C_6H_5NH_3SnBr_3$.	Found.	
		A.	B.
Sn	26.28	26.19	52.56
Br	52.93	26.06	52.85

All efforts to prepare other double bromides containing stannous tin, from solutions of varying proportions, were unsuccessful. The salt $C_6H_5NH_3SnBr_3$ was always formed or else the tin was oxidized to the stannic condition, oxidation always taking place when the solution was allowed to stand for any length of time.

Dianiline Bromostannate, $(C_6H_5NH_3)_2SnBr_6$.—This salt was formed by mixing hot solutions of aniline hydrobromide and stannic bromide in the portions of 2 molecules of aniline hydrobromide to 1 of stannic bromide, or with a larger portion of the stannic bromide. It was also formed when a solution of stannous bromide and aniline hydrobromide (when the aniline hydrobromide is not in excess of the proportions given above) was allowed to stand. It formed flat, tabular, straw-colored crystals. It was soluble in water, forming a milky precipitate upon standing for any length of time. The salt was readily soluble in alcohol, and less soluble in ether and chloroform. It began to sublime, with decomposition, at 250°.

An analysis of the salt gave :

	Calculated for $(C_6H_5NH_3)_2SnBr_6$.	Found.	
		A.	B.
Sn	15.12	15.05	15.11
Br	60.95	60.81	60.92

Tetraniline Bromostannate, $(C_6H_5NH_3)_4SnBr_8$.—This salt was formed by mixing solutions of aniline hydrobromide and stannic bromide in the proportions indicated by the formula, or by allowing solutions of stannous bromide, in which there was an excess of aniline hydrobromide, to stand.

The salt crystallized out in well-formed light-yellow crystals, soluble in alcohol, slightly soluble in ether and in chloroform. It was less soluble in water than the dianiline bromostannate, and crystallized out first from a solution containing both salts. It melted with decomposition at 274°.

Analysis of the salt gave:

	Calculated for $(C_6H_5NH_3)_4SnBr_8$.	Found.	
		A.	B.
Sn	10.48	10.35	10.42
Br	56.35	56.39	56.24

Stanford University, Cal.,
October 3, 1899.

Contributions from the Chemical Laboratory of Harvard College.

CXVI.—ON THE CONSTITUTION OF α-DIBROMDINITROBENZOL—PARADIBROMORTHODINITROBENZOL.

By D. F. Calhane and P. M. Wheeler.

When paradibrombenzol is treated with a mixture of fuming nitric acid and strong sulphuric acid the product consists of several isomeric dibromdinitrobenzols, some of which have been investigated by Austen,[1] who succeeded in isolating two of them, α-dibromdinitrobenzol, melting at 159°, and β-dibromdinitrobenzol, melting at 99°–100°. After studying[2] several derivatives of the β-compound he established[3] its constitution ($Br1.NO_22.Br4.NO_26$) by converting it into the parabromdinitrophenol ($OH1.NO_22.Br4.NO_26$). The α-compound, on the other hand, occurred in so much smaller quantity that he was unable to settle its constitution definitely, although he made progress in this direction by converting it into a paradibromnitraniline by the action of alcoholic ammonia. A replacement, such as this, of one nitro group in a dinitro body by an amino group, does not prove that the two nitro groups are in the ortho position to each other, as was supposed by Laubenheimer,[4] since Lobry de Bruyn[5] has shown in a number of papers that such reactions take place easily with paradinitro compounds and also with trinitro bodies of various structure. They prove nothing, therefore, regarding the constitution of the aromatic substances which take part in them, and the question of the constitution of α-dibromdinitrobenzol must be considered an open one.

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[1] Ber. d. chem. Ges., **9**, 621.

[2] *Ibid.*, 918.

[3] Am. J. Sci. (Silliman's), [3] **16**, 46.

[4] Ber. d. chem. Ges., **9**, 1827; **11**, 1155.

[5] Rec. trav. chim. Pays-Bas., **9**, 190, 208, 211 (1890); **13**, 118, 148 (1894).

The study of the paradibromdinitrobenzols was undertaken in the hope of throwing more light on the replacement of bromine by hydrogen in reactions between bromdinitrobenzols and sodic ethylate, which has been studied now for some years in this laboratory. The present paper has not carried the work further than the preliminary step of establishing the constitution of the α-isomer, but the investigation will be extended to the reactions of this body and the study of the other isomers.

To determine its constitution the α-dibromdinitrobenzol was reduced with a mixture of acetic acid and zinc dust to a dibromphenylenediamine, melting at 94°–95°. The bromine was then removed from this by prolonged treatment with sodium amalgam and water, when a small quantity of orthophenylenediamine was obtained. This result was confirmed by treating the paradibromphenylenediamine with phenanthrenequinone, which gave a paradibromphenanthrophenazine, or paradibromdiphenylenechinoxaline,

$$C_6H_2Br_2N_2C_2(C_6H_4)_2,$$

which melts at 297°; and also by treating it with benzil, from which was obtained the paradibromdiphenylchinoxaline,

$$C_6H_2Br_2N_2C_2(C_6H_5)_2,$$

melting at 215°–216°. As such chinoxalines are formed only from orthodiamines, it follows from all our observations that the two amino groups, and consequently the two nitro groups are in the ortho position to each other; and, as the substance was made from paradibrombenzol, it must be the paradibromorthodinitrobenzol ($Br1.NO_22.NO_23.Br4$). Our work, therefore, shows that the structure assigned to it by Austen is correct. We may add that the paradibromdiamine seemed also to give with benzaldehyde the characteristic reaction of an orthodiamine, but as the constitution was already sufficiently proved we did not pursue this work further.

The main object of the research—the study of the reaction of the paradibromorthodinitrobenzol must be postponed for the present, as the amount of this isomer formed is so small that our whole supply was used up in the determination of its constitution. The following preliminary experiments show that it is a reactive substance and that there is promise of interesting derivatives; sodic ethylate acted upon it even in the cold, as shown by the appearance of a deep-red color and the formation of both sodic bromide and sodic nitrite. Sodium malonic ester in the cold also gave a red coloration, and sodic bromide but no nitrite was formed.

EXPERIMENTAL PART.

The α-paradibromdinitrobenzol used in this work was prepared by the method of Austen[1] as follows: 200 grams of paradibrombenzol (made according to Jannasch[2]) were dissolved in 650 grams of fuming nitric acid (sp. gr. 1.505), and mixed with the same volume of strong sulphuric acid. Disregarding the red oil precipitated in this way, the mixture was warmed, when a violent reaction took place, during which the heat was removed. After this had come to an end the liquid was boiled gently for three hours in a flask closed with a porcelain crucible. It was then allowed to cool, and, before the oil had solidified, poured into a large quantity of water contained in an evaporating dish for convenience in removing the solid, which formed after standing over night. The crude product freed from acid by washing with water amounted to 246 grams instead of 275 grams; that is, 90 per cent of the theoretical yield.

In order to separate the isomers the crude product was recrystallized from glacial acetic acid, as recommended by Austen, when we found that the α-isomer could be obtained with but little difficulty by using the proper amount of the solvent. For this purpose 50 grams of the dry mixture were dissolved in 85 cc. of glacial acetic acid, and the solution was allowed to stand over night in a cool place. (The temperature of the laboratory was too high to give a copious crystallization.) From four such solutions, containing 200 grams of the crude product in all, 12.5 grams of crystals were obtained which melted at 152°. These 12.5 grams of substance were dissolved by heat in 50 cc. of glacial acetic acid, and after standing for two hours yielded 9.5 grams of crystals melting at 159°, and, therefore, pure α-paradibromdinitrobenzol. From the mother-liquors 2 grams more of pure substance were obtained, making 11.5 grams in all from 200 grams of the crude product, or 5.75 per cent. The amount of the α-isomer formed is, of course, larger than this, as a considerable portion of it must have remained mixed with the β-isomer in the mother-liquors; but our results confirm the observation of Austen that the α-isomer forms but a small part of the product of the reaction. The α-dibromdinitrobenzol forms colorless prisms with a vitreous luster. It was analyzed for greater surety, and gave 48.96 per cent of bromine instead of the 49.08 per cent calculated from the formula.

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[1] Ber. d. chem. Ges., 9, 621.

[2] *Ibid.*, 10, 1355.

Reduction of α-Paradibromdinitrobenzol.

One gram of the α-paradibromdinitrobenzol, mixed with 25–30 cc. of acetic acid containing 70 per cent of glacial acetic acid, was treated in a flask with 2 grams of zinc dust, and 2 grams more of zinc dust were added later in small portions with 10–15 cc. more of the acid. During the reduction it was found best to keep the temperature at about 60°–70° by allowing the flask to stand on a steam radiator, but as the dilute acetic acid had only a slight solvent action on the nitro compound, the mixture was heated from time to time more strongly on the water-bath. The action was finished when all the substance had gone into solution, forming a mahogany-brown liquid, which usually took place in from two to three hours. The solution was then allowed to cool, when it deposited large crystals of zincic acetate, which, after standing for some time, were filtered out and washed with more of the acetic acid till white. The dark-colored filtrate was diluted with a large volume of water which threw down the free base as a pinkish-brown gelatinous mass. The liquid with the precipitate suspended in it was then distilled with steam, when in some cases the base came over after a few minutes in a nearly pure state. In other cases it was necessary to distil off about two-thirds of the liquid before any of the amine appeared, but, if then the distillation was interrupted, and the contents of the flask diluted, a heavy precipitate was obtained, and after this the amine distilled over freely. It took usually two hours to drive over the whole of the base. The distillation must not be run too rapidly, as in that case the product was contaminated with a yellow oil, and throughout the process care must be taken to avoid the clogging of the condenser by the solid portion of the distillate. When the distillation ran successfully the amine formed a white gelatinous mass, which, on filtering, shrank very much, and was seen to be a felted collection of slender needles. It was filtered at once, and should be dried by pressing between filter-paper and standing in the desiccator as soon as possible, since it turns brown quickly if left in contact with water. The yield was on the average 0.75 gram from 1 gram instead of 0.82 gram; that is, 92 per cent of the theory. The yield was increased somewhat by dissolving the crystals of zincic acetate, mentioned above, in water, extracting with benzol, and precipitating the chloride of the base from the benzol solution by passing gaseous hydrochloric acid through it; but the amount obtained in this way was so small that it did not pay for the time and labor expended.

As crystallization from hot water partially decomposed the base, as was shown by the appearance of a brown color, and as it was so soluble in the organic solvents that we could not purify it by crystallization from these, the substance was prepared for analysis only by the distillation with steam, as already described. It was dried *in vacuo* and analyzed with the following result:

0.2592 gram of the substance gave, by the method of Carius, 0.3641 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Found.
Br	60.15	59.77

The base is, therefore, a dibromphenylenediamine, in which, as is proved later in this paper, the two atoms of bromine are in the para, and the two amino groups in the ortho, position to each other.

Properties of Paradibromorthophenylenediamine, $C_6H_2Br_2(NH_2)_2$.—As obtained by distillation with steam it forms a felted mass of small white needles. By careful crystallization from water it can be obtained sometimes in radiating groups of long white needles, looking like thistle-down. From alcohol it crystallizes in flat groups of short radiating needles. On long exposure to the air it turns light-brown, and this change in color takes place much more rapidly, even in a few hours, if the substance is moist or suspended in water. It melts at 94°–95°, and can be sublimed, but this process is too destructive to be used to advantage in its purification. It distils with steam and is very soluble in alcohol, ether, benzol, acetone, or chloroform; slightly soluble in cold water, more soluble in hot, but crystallization from this solution is almost invariably attended by decomposition, as shown by the appearance of a brown color. It shows weak basic properties. It dissolves easily in glacial acetic acid, and is thrown down apparently unaltered by dilution. Hot strong hydrochloric acid or hydrobromic acid dissolves it, and, on cooling, white needles of the corresponding salt are deposited; but, if the pure salt is needed, it is better to make it by passing the gaseous acid through a solution of the diamine in benzol, as described in the next section. Cold strong nitric acid dissolves it with a deep-red color, and on dilution a purple-red amorphous precipitate was thrown down. It is insoluble in cold, soluble in hot strong sulphuric acid, but this solution deposits nothing on dilution or cooling. Alkalies do not dissolve it, but promote its decomposition. Bromine gives a red oily precipitate with a solution of the diamine in acetic acid. The best way of purifying the paradibromorthophenylenediamine is by careful distillation with steam.

Chloride of Paradibromorthophenylenediamine, $C_6H_2Br_2NH_2NH_3Cl$.—This salt was made by dissolving the free base in anhydrous benzol, and passing dry hydrochloric acid through the solution, when it appeared as a pale-pink, amorphous precipitate. After filtering off the benzol it was purified by one recrystallization from hot concentrated hydrochloric acid, dried by pressing between filter-papers, and analyzed with the following result:

0.1760 gram of the substance gave, by the method of Carius, 0.3036 gram of a mixture of argentic chloride and argentic bromide.

	Calculated for $C_6H_2Br_2NH_2NH_3Cl$.	Found.
Cl and Br	64.63	64.91

Properties.—The salt, as precipitated from a benzol solution of the base with hydrochloric acid, forms a pinkish-white, amorphous powder, but appears in white, sparkling needles when crystallized from concentrated aqueous hydrochloric acid. When heated it decomposes, hydrochloric acid escapes, and the free base sublimes. The same decomposition takes place more slowly at ordinary temperatures. It is insoluble in cold water, and is broken up by hot water into the free base and hydrochloric acid; insoluble in benzol.

Paradibromorthophenylenediacetamide, $C_6H_2Br_2(NHCOCH_3)_2$.—This substance was obtained by heating the paradibromorthophenylenediamine for five minutes with acetic anhydride. The clear solution deposited nothing on cooling, but after treatment with water and neutralization with potassic hydrate a heavy white precipitate was formed, which was purified by crystallization from hot alcohol, dried at 150°, and analyzed with the following result:

0.1774 gram of the substance gave, by the method of Carius, 0.1929 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NHCOCH_3)_2$.	Found.
Br	45.71	46.28

The substance therefore is the diacetyl compound of the diamine, as would be expected from the work of Bistrzycki and Ulffers.[1]

Properties.—It crystallizes from hot alcohol in white, thread-like crystals matted together into a mass. It melts between 265° and 269° with decomposition, and is soluble in hydrochloric acid, alcohol, or glacial acetic acid; insoluble in hot water.

Conversion of α-Paradibromphenylenediamine into Orthophenylenediamine.

The paradibromphenylenediamine, obtained by the reduction of α-paradibromdinitrobenzol, as described above, was suspended in water in a flask and treated with sodium amalgam at ordinary temperatures in a stream of carbonic dioxide, which served to protect the solution from the air and to convert the sodic hydrate formed into sodic carbonate. After the reaction had gone on for three weeks a portion of the solution was tested with chlorine water and bisulphide of carbon, when a strong test for bromine was obtained. The mixture was then shaken with chloroform, and the chloroform extract yielded, on evaporation, a yellow oil, which was dissolved in hot water. This aqueous solution deposited, on evaporation, white plates, which were free from bromine, dissolved in hydrochloric acid, and melted at 100°. Orthophenylenediamine melts at 102° but, although the amount of our crystals was too small to see if the melting-point could be raised by recrystallization, there can be no doubt that our diamine was the ortho compound. It also gave with a concentrated solution of ferric chloride the characteristic deep-red color. Our inference that this product was orthophenylenediamine was confirmed by the following experiments:

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[1] Ber. d. chem. Ges., **23**, 1876 (1890).

Action of the α-Dibromphenylenediamine with Phenanthrenequinone. Paradibromphenanthrophenazine, or Paradibromdiphenylenechinoxaline.—To study this action 0.2 gram of the diamine were dissolved in alcohol and mixed with somewhat less than the calculated amount of phenanthrenequinone dissolved in hot glacial acetic acid. A flocculent lemon-yellow precipitate was deposited at once, which, after being washed and dried, was purified by crystallization from boiling benzol, dried at 100°, and analyzed with the following results:

I. 0.1993 gram of the substance gave, by the method of Carius, 0.1735 gram of argentic bromide.

II. 0.2783 gram of the substance gave, by the method of Carius, 0.2412 gram of argentic bromide.

	Calculated for $C_{20}H_{10}Br_2N_2$.	Found. I.	II.
Br	36.53	37.03	36.88

These analyses prove that this substance is the expected chinoxaline or azine, $C_6H_2Br_2N_2C_2(C_6H_4)_2$, formed by the removal of two molecules of water from the diamine and the quinone.

Properties of Paradibromphenanthrophenazine or Paradibromdiphenylenechinoxaline.—It crystallizes from benzol in slightly radiating bunches of silky yellow needles. It melts at about 297°, and is practically insoluble in cold, sparingly soluble in hot ethyl or methyl alcohol ; insoluble in cold ligroin or acetone, very sparingly soluble in either of these solvents when hot ; sparingly soluble in ether or glacial acetic acid ; somewhat soluble in benzol or chloroform, especially if hot ; insoluble in water. Strong hydrochloric acid, whether cold or hot, gives no apparent action, which is extraordinary, as Hinsberg[1] has found that the phenanthrophenazine gives a deep-red color with all the mineral acids, and the only difference between his compound and ours is that ours contains two atoms of bromine in place of two of hydrogen. This difference in behavior disappears, however, when the action of strong sulphuric acid is studied, as this converts our chinoxaline, even in the cold, into a dark claret-colored soluble substance. Strong nitric acid had no apparent action in the cold, but, if heated with the chinoxaline, dissolved it slowly with a reddish color. Fuming nitric acid dissolved it at once in the cold with a deep, wine-red color, and on dilution a new substance was precipitated. Sodic hydrate, whether cold or boiling, had no apparent effect on the substance. The best solvent for it is boiling benzol, or chloroform, but it is not freely soluble even in the latter.

Action of α-Dibromphenylenediamine with Benzil. Paradibromdiphenylchinoxaline.—To try this action, strong hot alcoholic solutions of the diamine and benzil were mixed in such proportions that there was a little more than 1 molecule of the diamine for each molecule of benzil. The reaction took place less easily than the corresponding one with phenanthrene quinone, for, whereas that acted in the cold, in this case it was necessary to heat in a flask with a return condenser for half to three-quarters of an hour in order to bring the reaction to an end. As the solution cooled the product crystallized out in bunches of white needles, which were so nearly pure that only one crystallization from alcohol and a little benzol was necessary to raise it to its constant melting-point, 215°–

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[1] Ann. Chem. (Liebig), 237, 340.

216°. It was then dried at 100° and analyzed with the following result:

0.2187 gram of the substance gave, by the method of Carius, 0.1890 gram of argentic bromide.

	Calculated for $C_{20}H_{12}Br_2N_2$.	Found.
Br	36.36	36.77

The substance is therefore paradibromdiphenylchinoxaline, $C_6H_2Br_2N_2C_2(C_6H_5)_2$.

Properties.—The chinoxaline crystallizes in sheaf-shaped bunches of long, white, somewhat curved and branched, needles, which, when better developed, appear under the microscope, as slender prisms, sometimes terminated by a single plane, sometimes bluntly pointed. It melts at 215°–216°, and is readily soluble in ether, benzol, chloroform, acetone, or carbon disulphide; nearly insoluble in cold ethyl or methyl alcohol, sparingly soluble when they are hot; sparingly soluble in cold ligroin, readily in it when hot; slightly soluble in cold glacial acetic acid, soluble in it when hot. Strong hydrochloric acid has no apparent action on it either hot or cold, whereas the corresponding unsubstituted compound forms a salt with hydrochloric acid. Cold strong sulphuric acid dissolves it easily with a claret-red color. Cold, strong nitric acid also dissolves it with a lemon-yellow color, and fuming nitric acid acts in the same way. Sodic hydrate, whether cold or hot, has no action upon it. The best solvent for it is alcohol mixed with a little benzol.

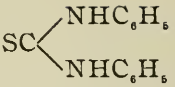
The research will be continued in this laboratory and extended to the other isomeric dibromdinitrobenzols formed at the same time with the body studied in this paper.

Contributions from the Chemical Laboratory of Cornell University.

PHENYL MUSTARD OIL AS A REAGENT FOR THE DETECTION OF THE ALCOHOLIC HYDROXYL GROUP.

By W. R. Orndorff and F. A. Richmond.

Phenyl isocyanate, $C_6H_5N{=}C{=}O$, combines very readily with alcohols, phenols, and oximes to form urethanes, and with substituted ammonias to give derivatives of urea. Indeed, the fact that it reacts so easily, without the formation of by-products, and that the compounds formed are readily purified and analyzed, makes this substance a very valuable reagent in the organic chemical laboratory for the detection of the groups characteristic of the above-mentioned classes of compounds. Unfortunately, the substance is no longer made on the large scale in the factory and it is not easy to make in any quantity in the laboratory. Its high cost and the difficulty of preparing the substance have therefore prevented its coming into general use. The analogously constituted compound, phenyl mustard oil, $C_6H_5N{=}C{=}S$, can be readily made in the laboratory and is a comparatively cheap substance. If it should be found to react as readily as phenyl isocyanate with the classes of organic compounds above enumerated, and could be substituted for this substance, much would therefore be gained. With this idea in view, the following investigation of the action of phenyl mustard oil on alcohols and phenols was undertaken. It was soon found, however, that phenyl mustard oil reacts much less readily than phenyl isocyanate, so that it is highly improbable that it will ever replace this substance as a reagent in the chemical laboratory. With monacid alcohols of the paraffin series, primary, secondary, and tertiary, it reacts to form well-crystallized thiourethanes, but it does not combine with unsaturated alcohols, polyacid alcohols, phenols or alcohols of the benzene series to form similar compounds. It does not combine with acids of the paraffin or the benzene series. Its use as a reagent for the detection of the hydroxyl group is therefore limited to the monacid alcohols of the paraffin series.

The only statements found in the literature regarding the action of phenyl mustard oil on alcohol and phenols are those of A. W. von Hofmann[1] and others[2] describing the product of the action of phenyl mustard oil on ethyl alcohol, of A. E. Dixon[3] and later of H. Lloyd Snape[4] on the action of phenyl mustard oil on phenols, and of Tessmer and Volkmann[5] on the formation of diphenyl thiourea,  $SC\begin{cases}NHC_6H_5\\NHC_6H_5\end{cases}$, when phenyl mustard oil and glycerin are heated together.

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[1] Ber. d. chem. Ges., **2**, 120; **3**, 772.

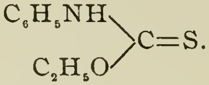
[2] See Lehrbuch der Organischen Chemie, V. Meyer u. P. Jacobson, II, **1**, 203.

[3] J. Chem. Soc., **57**, 268.

[4] *Ibid.*, **69**, 98.

[5] Ber. d. chem. Ges., **18**, 972.

Hofmann heated molecular proportions of phenyl mustard oil and absolute alcohol in a sealed tube to a temperature of 110°–115° C. for three hours. The product, on recrystallization from alcohol, consisted of white crystals melting at 65° C. To this product Hofmann assigns the following structural formula:



$$\left.\begin{matrix}C_6H_5NH\\C_2H_5O\end{matrix}\right\rangle C{=}S.$$

A much simpler method of making this phenyl thiourethane is given in Meyer and Jacobson's Organische Chemie, II, 1, 203. According to these authors it is formed extraordinarily easily by simply boiling phenyl mustard oil with four times its weight of absolute alcohol for several hours.

Dixon heated phenol and phenyl mustard oil in sealed tubes to 140°–150° C., and obtained a product crystallizing in octahedra, which resembled sulphur in appearance and color and melted at 149°–151° C. A determination of the amount of sulphur in this compound gave 13.48 per cent, while the theory for $C_6H_5NH.CS.OC_6H_5$ requires 13.97 per cent of sulphur. Later Snape obtained the same compound by a similar method, but he heated his tubes to a higher temperature and for a longer time, and obtained a larger yield of material. He describes his product as crystallizing from absolute alcohol in yellow leaves or needles melting at 148° C. Like Dixon, he merely determined the amount of sulphur in this compound and found 14.03 per cent. Snape further attempted to effect a combination of phenyl mustard oil with resorcin, hydroquinone, and glycol, but without success.

From the ease with which phenyl mustard oil reacts with ethyl alcohol[1] we expected it would react with all alcohols in a manner analogous to that of phenyl isocyanate forming, instead of urethanes, thiourethanes. These thiourethanes could be very readily analyzed by the Kjeldahl method for nitrogen and by the Carius method for sulphur, and if these two determinations checked, the composition of the substance would be determined as accurately as if a complete combustion analysis had been made. These thiourethanes are also acid in their nature and form very readily with an alcoholic, ammoniacal solution of silver oxide, a silver salt, which probably has the following composition :[1]

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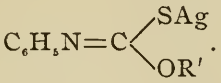
[1] These two substances unite when they are mixed and allowed to stand for some time at the room temperature.

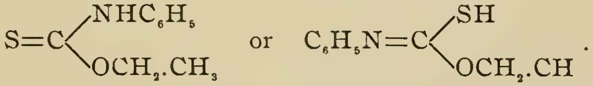


$$C_6H_5N{=}C\begin{matrix}\diagup SAg\\ \diagdown OR'\end{matrix}.$$

These silver salts are easily purified and analyzed, and from the amount of silver found it is easy to calculate the composition of the thiourethane, thus doing away with the longer determinations of the amounts of nitrogen and sulphur and simplifying the method very much.

We give below the results of our experiments with the various alcohols and phenols used.

The Compound of Phenyl Mustard Oil with Ethyl Alcohol (*Ethyl Phenyl Sulphocarbamate*),



$$S{=}C\begin{matrix}\diagup NHC_6H_5\\ \diagdown OCH_2.CH_3\end{matrix} \quad \text{or} \quad C_6H_5N{=}C\begin{matrix}\diagup SH\\ \diagdown OCH_2.CH\end{matrix}.$$

This compound, which, as already stated, was first made and described by Hofmann, was prepared as follows : 5 grams of pure phenyl mustard oil, having a constant boiling-point of 222° C., were heated with a slight excess of absolute alcohol in a sealed tube to a temperature of 110°–115° C. for three hours. After cooling, the tube was found to contain a solid substance which, on recrystallization from alcohol, gave beautiful white prisms, melting at 71°–72°. A crystallographic examination of these crystals by Mr. J. E. Gignoux, under the direction of Prof. A. C. Gill, of the mineralogical department of this university, showed their complete identity with the crystals of ethyl phenylsulphocarbamate made by Hofmann and measured by Groth. Later we adopted the method of preparation given by V. Meyer and P. Jacobson and mentioned above.

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[1] In this formula R' represents any univalent alcoholic radical like CH_3, C_2H_5, etc.

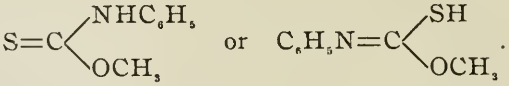
From this ethyl phenylsulphocarbamate we made the silver salt according to the method given by Liebermann[1] and analyzed this. The following results were obtained.[2]

I. 0.3242 gram substance gave 0.1216 gram Ag.
II. 0.3847 gram substance gave 0.1446 gram Ag.

	Calculated for $C_6H_5N{=}C\langle\begin{smallmatrix}SAg\\OC_2H_5\end{smallmatrix}$.	Found. I.	II.
Ag	37.45	37.50	37.58

The above results show that phenyl mustard oil and ethyl alcohol combine very readily to form ethyl phenylsulphocarbamate. The substance crystallizes very beautifully in the triclinic system, is insoluble in water, soluble in alcohol, ether, chloroform, benzene, acetone, carbon bisulphide, and acetic ether, and melts at 71°–72° C. When heated to its boiling-point it decomposes into phenyl mustard oil and alcohol, forming at the same time both thiocarbanilide (diphenyl thiourea, $S{=}C\langle\begin{smallmatrix}NHC_6H_5\\NHC_6H_5\end{smallmatrix}$), and carbanilide diphenyl urea $O{=}C\langle\begin{smallmatrix}NHC_6H_5\\NHC_6H_5\end{smallmatrix}$), as stated by Hofmann.

The Compound of Phenyl Mustard Oil with Methyl Alcohol (Methyl Phenylsulphocarbamate),



$$S{=}C\langle\begin{smallmatrix}NHC_6H_5\\OCH_3\end{smallmatrix} \quad \text{or} \quad C_6H_5N{=}C\langle\begin{smallmatrix}SH\\OCH_3\end{smallmatrix}.$$

The methods employed in making this compound were similar to those used in making the ethyl compound. On recrystallization from alcohol white crystals were obtained, melting at 97° C., insoluble in water and easily soluble in alcohol, ether, chloroform, acetone, benzene, and acetic ether. Analysis gave the following results :

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[1] Ann. Chem. (Liebig), **207**, 142.

[2] The atomic weights used in this paper are those given by F. W. Clarke in the new edition of his "Recalculation of the Atomic Weights" (1897).

Determination of the Amount of Nitrogen (*Kjeldahl Method*).

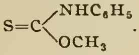
I. 0.5159 gram substance gave 0.05256 gram NH_3, corresponding to 0.04329 gram N.

II. 1.3218 gram substance gave 0.13223 gram NH_3, corresponding to 0.1089 gram N.

Determination of the Amount of Sulphur (*Carius Method*).

I. 0.1268 gram substance gave 0.1775 gram $BaSO_4$.

II. 0.2330 gram substance gave 0.3263 gram $BaSO_4$.

	Calculated for  $S{=}C(NHC_6H_5)(OCH_3)$.	Found. I.	Found. II.
N	8.397	8.238	8.39
S	19.175	19.225	19.223

These results show that the compound has the composition of the methyl ester of phenylsulphocarbamic acid, and that methyl alcohol reacts very readily with phenyl mustard oil.

A crystallographic examination of the crystals of this compound by Mr. J. E. Gignoux gave the following results:

Crystal system, triclinic, probably hemihedral (pedial class of Groth).

The crystals are usually thin plates, parallel to the face taken as the basal pinacoid.

From measurements on 31 crystals the values established for the crystallographic constants were:

$\alpha = 63° 19' 57''$, $\beta = 128° 52' 50''$, $\gamma = 103° 8' 48''$.

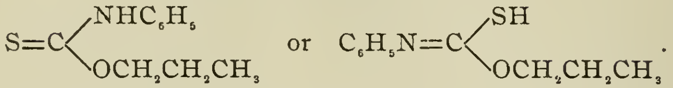
$a : b : c = 0.6065 : 1 : 0.5513$.

The principal angles for the identification of the substance would thus be:

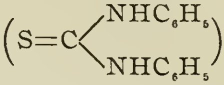
$$001 : 100 = 57° 24' 8''$$
$$001 : 010 = 108° 37' 41''$$
$$010 : 100 = 99° 59' 23''$$

In addition to the three pinacoids whose angles have just been given, the faces $\infty\overset{|}{P}(1\bar{1}0)$; $2{,}P(2\bar{2}\bar{1})$; ${,}P{,}\bar{\infty}(10\bar{1})$; and $\frac{4}{3}{}'P{,}\breve{\infty}(04\bar{3})$ were observed. Of these the first two never showed a parallel (with the exception of a poorly developed one in a single instance); hence the presumption that the crystals are hemihedral.

The Compound of Phenyl Mustard Oil with Propyl Alcohol (Propyl Phenylsulphocarbamate),



$$S{=}C\begin{cases}NHC_6H_5\\OCH_2CH_2CH_3\end{cases} \quad \text{or} \quad C_6H_5N{=}C\begin{cases}SH\\OCH_2CH_2CH_3\end{cases}.$$

Attempts were made to prepare this compound by heating molecular quantities of the mustard oil and propyl alcohol, in sealed tubes, at temperatures varying from 110° to 250° C., for periods of from three to six hours, but without success. In every case gaseous products were formed together with a quantity of thiocarbanilide  $\left(S{=}C\begin{cases}NHC_6H_5\\NHC_6H_5\end{cases}\right)$. After varying the conditions in many ways we finally found that the compound could be readily formed by heating the mustard oil and alcohol, in a flask provided with a return condenser, to the temperature of a boiling water-bath for several hours. Five grams of phenyl mustard oil and 5 grams of the pure normal propyl alcohol were thus heated for sixteen hours. The straw-colored liquid still had the odor of propyl alcohol, but on allowing it to stand in the cold it deposited long, white needles. These were filtered off, dissolved in benzene (in order to remove thiocarbanilide, which is practically insoluble in cold benzene), the benzene evaporated off, and the product recrystallized from absolute alcohol. The substance crystallizes in white needles belonging to the triclinic system, which melt at 48° C. It is easily soluble in alcohol, ether, chloroform, acetone, benzene, and acetic ether. Analyses gave the following results :

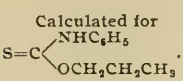
Determination of Nitrogen (Kjeldahl Method).

I. 0.4836 gram substance gave 0.04163 gram NH_3, corresponding to 0.03429 gram N.

II. 0.6087 gram substance gave 0.05217 gram NH_3, corresponding to 0.04297 gram N.

Determination of Sulphur (Carius Method).

I. 0.1956 gram substance gave 0.2341 gram $BaSO_4$.
II. 0.2126 gram substance gave 0.2559 gram $BaSO_4$.

	Calculated for  $S=C\begin{matrix}\diagup NHC_6H_5\\ \diagdown OCH_2CH_2CH_3\end{matrix}$.	Found. I.	Found. II.
N	7.191	7.059	7.09
S	16.421	16.44	16.53

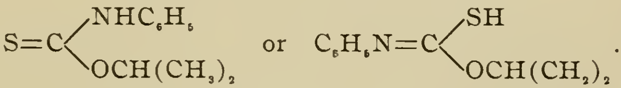
These results show that the compound is the propyl ester of phenylsulphocarbamic acid.

Mr. Gignoux reports as follows concerning the crystallography of this substance :

Crystal system, triclinic.

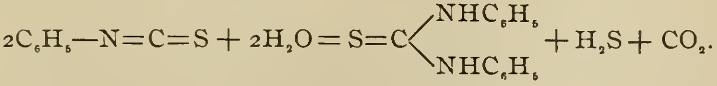
The bright, colorless crystals are of acicular habit. The needles are six-sided, being bounded by three pairs of faces, whose angles are 68° 29′, 72° 06′, and 39° 25′. No end faces could be observed even though crystals were made from a number of solvents, including acetone, benzene, ethyl alcohol, amyl alcohol, and acetic ether. Since the extinction angle is oblique, however, the crystals can be definitely said to be triclinic even in the absence of terminal planes.

The Compound of Phenyl Mustard Oil with Isopropyl Alcohol (Isopropyl Phenylsulphocarbamate),



$$S=C\begin{matrix}\diagup NHC_6H_5\\ \diagdown OCH(CH_3)_2\end{matrix} \quad \text{or} \quad C_6H_5N=C\begin{matrix}\diagup SH\\ \diagdown OCH(CH_2)_2\end{matrix}.$$

Attempts were first made to prepare this compound by heating the components together in sealed tubes at varying temperatures, but without success. In every case thiocarbanilide, $S=C(NHC_6H_5)_2$, was the only solid product obtained. At the same time gaseous products were formed in considerable amount. This formation of diphenyl thiourea is probably due to the reaction between the phenyl mustard oil and the water formed from the alcohol. The alcohol, by loss of water, forms the ether (dipropyl ether) or the unsaturated hydrocarbon (propylene), and the phenyl mustard oil reacts with the water as follows :



$$2C_6H_5—N=C=S + 2H_2O = S=C\begin{matrix}\diagup NHC_6H_5\\ \diagdown NHC_6H_5\end{matrix} + H_2S + CO_2.$$

Using the same method which we employed in the case of propyl alcohol, and heating for twenty hours, we succeeded in preparing the compound without trouble. The light-yellow liquid obtained deposited, in the cold, white crystals which, when freed from thiocarbanilide by dissolving in benzene and recrystallizing from alcohol, melted at 85°.5 C. It crystallizes in the monoclinic system and is soluble in alcohol, ether, chloroform, benzene, carbon bisulphide, and acetic ether. The following results were obtained on analysis :

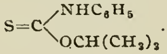
Determination of the Amount of Nitrogen (*Kjeldahl Method*).

I. 0.3716 gram substance gave 0.03216 gram NH_3, corresponding to 0.02649 gram N.

II. 0.3788 gram substance gave 0.03284 gram NH_3, corresponding to 0.02705 gram N.

Determination of the Amount of Sulphur (*Carius Method*).

0.2082 gram substance gave 0.2493 gram $BaSO_4$.

	Calculated for	Found.	
	 $S{=}C\begin{matrix}\diagup NHC_6H_5\\ \diagdown OCH(CH_3)_2\end{matrix}$.	I.	II.
N	7.191	7.129	7.14
S	16.421	16.44	...

These results show that the substance is isopropyl phenylsulphocarbamate and that phenyl mustard oil reacts with secondary propyl alcohol as readily as it does with the primary alcohols of the paraffin series.

Mr. Ginoux reports as follows concerning the crystals of this compound :

Crystal system, monoclinic.

The habit of the brilliant, colorless crystals is very varied, in general conforming to one of three types : *a*, pyramidal, with a small base ; *b*, columnar, with their elongation parallel to the à axis ; and *c*, six-sided tabular, with the base as the principal face. From the measurements on 21 crystals the crystallographic constants were determined to be :

$$\beta = 87^\circ\ 28'\ 50''. \quad \grave{a} : \bar{b} : \overset{|}{c} = 0.6777 : 1 : 1.8325.$$

The faces commonly present are +P,($\bar{1}$11) ; —P,(111) ; oP,(001) ; P$\grave{\infty}$,(011) ; ∞P,(110); and ∞P$\grave{\infty}$,(010).

The following are the angles :

$001 : 110 = 87^\circ\, 54'\, 52''$

$001 : \bar{1}11 = 74^\circ\, 53'\, 24''$

$001 : 111 = 71^\circ\, 04'\, 31''$

$001 : 011 = 61^\circ\, 21'\, 19''$

$\bar{1}11 : 111 = 104^\circ\, 42'\, 21''$

$\bar{1}11 : \bar{1}\bar{1}1 = 65^\circ\, 34'\, 54''$

$111 : 1\bar{1}1 = 64^\circ\, 06'\, 12''$

$111 : 110 = 16^\circ\, 17'\, 16''$

$\bar{1}11 : \bar{1}10 = 17^\circ\, 11'\, 44''$

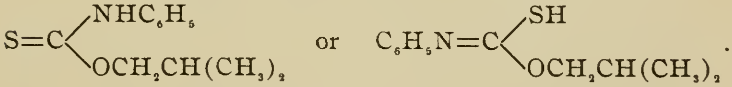
$111 : 011 = 51^\circ\, 35'\, 45''$

$\bar{1}11 : 011 = 53^\circ\, 06'\, 36''$

$010 : 011 = 28^\circ\, 38'\, 41''$

The monoclinic character of the crystals was confirmed by their optical behavior.

The Compound of Phenyl Mustard Oil with Isobutyl Alcohol (Isobutyl Phenylsulphocarbamate),



$$S{=}C\left\langle\begin{matrix}NHC_6H_5\\OCH_2CH(CH_3)_2\end{matrix}\right. \quad \text{or} \quad C_6H_5N{=}C\left\langle\begin{matrix}SH\\OCH_2CH(CH_3)_2\end{matrix}\right. .$$

The isobutyl alcohol used was a pure product which boiled at 107° C. Heating the alcohol and mustard oil in sealed tubes at temperatures varying from 110° to 180° C., gave no solid product except thiocarbanilide. We therefore tried the method used with propyl alcohol, heating the two substances together for twenty hours. On cooling the yellow liquid a white crystalline substance was deposited, which was freed from thiocarbanilide by means of benzene, and recrystallized from absolute alcohol. It is soluble in alcohol, ether, benzene, carbon bisulphide, and chloroform, insoluble in water, and melts sharply at 80°.5 C. Analyses gave the following results :

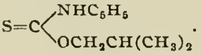
Determination of the Amount of Nitrogen (Kjeldahl Method).

I. 0.3469 gram substance gave 0.028402 gram NH_3, corresponding to 0.02339 gram N.

II. 0.2873 gram substance gave 0.02375 gram NH_3, corresponding to 0.01956 gram N.

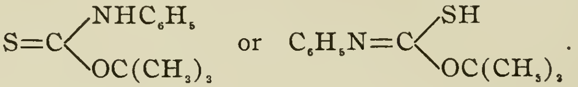
Determination of the Amount of Sulphur (*Carius Method*).

I. 0.1642 gram substance gave 0.1845 gram $BaSO_4$.
II. 0.1609 gram substance gave 0.1799 gram $BaSO_4$.

	Calculated for  $S=C\begin{array}{l}\diagup NHC_6H_5\\ \diagdown OCH_2CH(CH_3)_2\end{array}.$	Found.	
		I.	II.
N	6.709	6.74	6.809
S	15.321	15.43	15.35

The product is therefore isobutyl phenylsulphocarbamate.

The Compound of Phenyl Mustard Oil with Tertiary Butyl Alcohol (*Tertiary Butyl Phenylsulphocarbamate*),



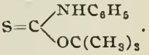
$$S=C\begin{array}{l}\diagup NHC_6H_5\\ \diagdown OC(CH_3)_3\end{array} \quad \text{or} \quad C_6H_5N=C\begin{array}{l}\diagup SH\\ \diagdown OC(CH_3)_3\end{array}.$$

The tertiary butyl alcohol used boiled constantly at 83° C. The method of heating the two substances together in sealed tubes gave in every case thiocarbanilide and no other solid product. Heating the two products together on the water-bath, in a flask provided with a return condenser, for twenty hours gave a yellowish liquid from which long white needles separated out when placed in a freezing-mixture. These crystals dissolved again when the mixture was brought into a room at ordinary temperature, and could not then be again obtained. More of the material was then made, placed in a freezing-mixture as before, and as soon as the crystals separated out they were dried as quickly as possible on filter-paper and transferred at once to a weighed tube, which, after re-weighing, was at once placed in the digestion flask. The following are the results of two analyses of this substance.

Determination of the Amount of Nitrogen (*Kjeldahl Method*).

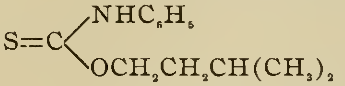
I. 0.8028 gram substance gave 0.060947 gram NH_3, corresponding to 0.050192 gram N.

II. 0.6221 gram substance gave 0.04808 gram NH_3, corresponding to 0.03959 gram N.

	Calculated for  $S=C\begin{array}{l}\diagup NHC_6H_5\\ \diagdown OC(CH_3)_3\end{array}.$	Found.	
		I.	II.
N	6.709	6.25	6.36

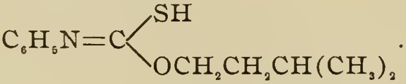
These results show that the compound is tertiary butyl phenylsulphocarbamate and that tertiary alcohols react with the phenyl mustard oil just as readily as the primary and secondary compounds do.

The Compound of Phenyl Mustard Oil with Isoamyl Alcohol (Isoamyl Phenylsulphocarbamate),



$$S{=}C\begin{cases}NHC_6H_5\\ OCH_2CH_2CH(CH_3)_2\end{cases}$$

or



$$C_6H_5N{=}C\begin{cases}SH\\ OCH_2CH_2CH(CH_3)_2\end{cases}.$$

The isoamyl alcohol used was carefully purified and boiled constantly at 131° C. The phenyl mustard oil and the isoamyl alcohol were heated to boiling for some hours. The yellow liquid deposited white crystals on standing in the cold. As these crystals melt at ordinary temperatures they were removed from the liquid and pressed between filter-paper in the cold. When dried as completely as possible they were washed with a little alcohol and again dried between filter-paper. The product was soluble in alcohol and ether and melted at approximately 21° C. Analyses gave the following results:

Determination of the Amount af Nitrogen (Kjeldahl Method).

I. 0.3550 gram substance gave 0.029106 gram NH_3, corresponding to 0.02397 gram N.

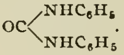
II. 0.3360 gram substance gave 0.02539 gram NH_3, corresponding to 0.02091 gram N.

	Calculated for $S{=}C\begin{cases}NHC_6H_5\\ OCH_2CH_2CH(CH_3)_2\end{cases}.$	Found. I.	II.
N	6.288	6.75	6.22

The substance is therefore isoamyl phenylsulphocarbamate.

We next heated phenyl mustard oil with allyl alcohol in order to see if unsaturated alcohols react in the same way as the monacid alcohols of the paraffin series. The yellowish liquid deposited, on standing in the cold, a white crystalline substance melting at 236° C., insoluble in water but soluble in alcohol and ether. This substance contained no sulphur, for when oxidized with nitric acid, according to the Carius method, it gave only a trace of barium sulphate. A determination of nitrogen by the Kjeldahl method gave the following result:

0.3113 gram substance gave 0.04755 gram NH_3, corresponding to 0.03916 gram N.

	Calculated for  $OC(NHC_6H_5)_2$.	Found.
N	13.2	12.57

From these results it will be seen that the substance is symmetrical diphenyl urea. This was further proved by a determination of the boiling-point of the substance, which was found to be 262° C. The melting-point of diphenyl urea is 235° and its boiling-point 260° C.

Allyl alcohol, therefore, does not react with phenyl mustard oil to form a thiourethane.

The reaction of phenyl mustard oil with glycol and glycerin was next tried in order to see if the phenyl mustard oil could be used as a reagent for detecting the alcoholic hydroxyl group in polyacid alcohols. In both cases the only solid product formed was thiocarbanilide, as was shown by the analyses of the substance and a determination of its physical properties, and comparison of these with those of diphenyl thiourea, $SC(NHC_6H_5)_2$. This result is in accord with that of Tessmer and Volkmann,[1] who state that phenyl mustard oil reacts with glycerin to give diphenyl thiourea, due to the water which splits off from the glycerin. It is also in accord with the work of Snape, who states that phenyl mustard oil does not react with glycol to form a thiourethane.

With neither erythrite nor glucose nor with glycol chlorhydrin does phenyl mustard oil react, so that this substance cannot be used to detect the alcoholic hydroxyl group in polyacid alcohols.

We next took up the reaction between phenyl mustard oil and the phenols. As stated in the introduction to this article, both Dixon and Snape claim to have prepared a compound of phenyl mustard oil with phenol, though Snape found it impossible to prepare compounds with resorcin or hydroquinone. We first endeavored to repeat the work of Dixon and Snape and to effect the union of the mustard oil and phenol by heating the two substances together in sealed tubes. In every case, however, the tubes broke owing to the great internal pressure. By heating the two substances together to boiling for thirty-two hours and allowing the dark-red, syrupy liquid to stand in the cold, yellow needles crystallized out which melted at 152° C. These, when recrystallized from alcohol, were nearly white. They are nearly insoluble in ether and petroleum ether, readily soluble in alcohol, chloroform, acetone, and acetic ether, but difficultly in benzene. An analysis of the product purified by recrystallization from alcohol gave the following results:

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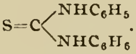
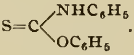
[1] Ber. d. chem. Ges., 18, 972.

Determination of Nitrogen by the Kjeldahl Method.

0.1390 gram substance gave 0.02095 gram NH_3, corresponding to 0.01726 gram N.

	Calculated for		Found.
	 $S{=}C\langle^{NHC_6H_5}_{NHC_6H_6}$.	 $S{=}C\langle^{NHC_6H_5}_{OC_6H_5}$.	
N	12.301	6.125	12.41
S	14.04	13.97	....

This compound is therefore thiocarbanilide and not the phenyl ester of sulphocarbamic acid. From the description of the compound given by both Dixon and Snape it seems highly probable that they obtained this same compound. They describe the compound they obtained as crystallizing in yellow leaves or needles, insoluble in ether and light petroleum, which agrees with thiocarbanilide and with our compound. Dixon gives the melting-point of his compound as 149°–151° C., while Snape found his to melt at 148° C. The melting-point of our compound was 152°, while thiocarbanilide melts at 150°.5 according to Lellmann, and at 153° according to Bamberger.

Unfortunately, both Dixon and Snape only determined the amount of sulphur in their compounds. Dixon found 13.48 per cent of sulphur, while Snape obtained 14.03 per cent, results which agree with that required for either thiocarbanilide

(14.04), or the phenyl ester of phenyl sulphocarbamic acid (13.97).

From the properties of the substance we obtained, as well as from the results on analysis, there can be no doubt that the substance is thiocarbanilide, and it seems highly probable that both Dixon and Snape obtained the same compound.

We then tried to bring about the union of phenyl mustard oil with hydroquinone and pyrogallol, but without success. Phenyl mustard oil does not, therefore, combine with phenols to form thiourethanes.

The aromatic alcohols also do not combine with phenyl mustard oil to form thiourethanes, for even when heated together for thirty-nine hours benzyl alcohol and phenyl mustard oil underwent no change; at least, no solid product could be isolated from the liquid.

It seemed desirable, in connection with this investigation of the action of phenyl mustard oil on alcohols and phenols, to determine whether this substance would combine with the acids of the paraffin and benzene series to form thiourethanes. We therefore heated 5 grams of phenyl mustard oil and 3 grams of acetic acid together on a water-bath, at 100°, for twenty-four hours. The only solid product obtained was a white crystalline substance melting at 236° and boiling at 262°. This compound was insoluble in water, only slightly soluble in chloroform, ether, and benzene, but soluble in acetone and alcohol. It is probably, therefore diphenyl urea.

With benzoic acid phenyl mustard oil does not combine when heated together on the water-bath for twenty-five hours. The benzoic acid dissolves in the hot phenyl mustard oil but crystallizes out again on cooling. With ethylidene lactic acid, phenyl mustard oil gave no thiourethane. The only products isolated after heating the two substances together for forty hours were thiocarbanilide (m. p. 154° C.) and carbanilide (m. p. 236°, b. p. 262°).

Acids therefore do not combine with phenyl mustard oil to form thiourethanes.

JUNE, 1899.

ON THE EFFECT OF VARIOUS SOLVENTS ON THE ALLOTROPIC CHANGE OF MERCURIC IODIDE.

BY J. H. KASTLE AND MARY E. CLARK.

Several years ago, in endeavoring to find some method other than that of sublimation, for the preparation of the yellow modification of mercuric iodide, it was observed by one of us (Kastle) that it could be prepared by dissolving the ordinary red modification in boiling amyl alcohol and allowing the solution to cool. Somewhat later Mr. Kemper studied the solution of sulphur and mercuric iodide in several high-boiling hydrocarbon solvents, such as naphthalene and pseudo-cumene. He observed that the red mercuric iodide dissolved quite freely in these solvents, especially above the transition-temperature of the iodide, to form yellow solutions, from which the yellow modification invariably crystallized out on cooling. It therefore occurred to one of us that it would probably prove interesting to study the action of a number of solvents, high- and low-boiling, on this compound. Altogether the action of 24 solvents has been studied. These, together with their boiling-points, are as follows :

Name of substance.	Boiling-point.
Ethyl bromide	38.8
Propyl chloride	48.0
Acetone	56.0
Ethylidene chloride	60.0
Ethyl iodide	72.0
Ethyl acetate	76.0
Ethyl alcohol	78.3
Isopropyl bromide	60.0
Benzene	80.0
Allyl alcohol	96.0
Toluene	110.0
Ethyl cyanide	115.0
Ethyl butyrate	121.0
Ethyl isobutyrate	110.0
Ethyl propionate	99.0
Amyl alcohol	132.0
Benzoic acid	249.0
Phenol	181.5

Name of substance.	Boiling-point.
Benzene cyanide	208.0
Oil of wintergreen	117.0
Propyl bromide	71.0
Pseudo-cumene	169.8
Naphthalene	218.0
Salol	....

In what follows, unless expressly stated to the contrary, the solubility of mercuric iodide is given for the hot solvent. In most cases it refers to its solubility at the boiling-point of the solvent.

Ethyl Alcohol.—Mercuric iodide is moderately soluble in absolute alcohol at its boiling-point. The solution had a decided yellow color, and on being placed in a freezing-mixture (ice and salt), yellow crystals separated from the solvent. These soon changed to the red modification. In order to determine whether the yellow variety alone crystallized from the solution, a drop of the solution was placed on the watch-glass and examined under a microscope. As a result of a number of such observations it was found that the yellow variety only separated from the solution, subsequently changing more or less rapidly to the red.

Amyl Alcohol.—Mercuric iodide dissolves very freely in hot amyl alcohol. A moderately concentrated solution prepared near its boiling-point was allowed to cool gradually. At 100° C. a large crop of lemon-yellow crystals separated from the solution. As the solution cooled further crops of yellow crystals were obtained. At 67° C. the first change of color was noticeable. Under amyl alcohol the yellow mercuric iodide is moderately stable. In two hours the solution had cooled down to 40° C. and about half the yellow had changed. After sixteen hours at ordinary temperature nearly all of the yellow had altered.

Allyl Alcohol.—Allyl alcohol dissolves mercuric iodide very freely, much more so than ethyl alcohol. The solution is yellow. On sudden cooling a large crop of lemon-yellow crystals is obtained. These were mostly of the needle-shaped variety, with some perfect rhombs. The yellow variety slowly changed to red. On allowing the solution to cool gradually a large number of rhombic crystals were obtained.

Acetone.—Mercuric iodide was found to be only slightly soluble in this solvent, much less so than in ethyl alcohol. The solution was yellow in color. On cooling irridescent yellow plates separated from the solution and rapidly turned red.

Phenol.—At 150° C. phenol dissolved mercuric iodide tolerably freely. A partially saturated solution at this temperature was found to have a yellow color and to deposit crystals on gradually cooling to 40°–50° C. The iodide crystallized out in yellow rhombs, together with numerous elongated and small fragmentary crystals.

Benzene.—Mercuric iodide is readily soluble in boiling benzene. A saturated solution of the iodide in this solvent is yellow in color. On being placed in ice-water, the solution gave considerable quantities of yellow crystals. These yellow crystals changed to red with great rapidity under this solvent, as all of them were completely altered in from two to three minutes.

Toluene.—Mercuric iodide is more soluble in toluene than in ethyl alcohol—color of the solution deep yellow. On cooling the hot solution a yellow precipitate was thrown down. In the first portions of this no crystalline structure was visible, even under the microscope. The last portions of the compound which were obtained from the solution were crystalline. The yellow precipitate rapidly changed to red.

Naphthalene.—Mercuric iodide is readily soluble in naphthalene at temperatures above its transition-point. A solution saturated at 160° C. and cooled to 150° C. gave yellow crystals. The solution in napthalene is yellow.

Pseudo-cumene.—Mercuric iodide is readily soluble in hot pseudo-cumene, giving a yellow solution. A solution in pseudo-cumene saturated at 143° C. gives, on slow cooling, very large and perfect yellow crystals.

Ethyl Iodide.—Mercuric iodide was found to be readily soluble in this solvent. Taken altogether, it is probably the best solvent for this compound of any yet tried. The solution was intensely yellow. On placing it in a freezing-mixture it yielded a large crop of yellow irridescent plates, which closely resembled lead iodide in appearance. On microscopic examination these crystals were found to consist of a very large number of rhombs, together with a number of elongated rhombic plates. Under the solvent the yellow variety quickly changed to red. On the other hand, some of the yellow crystals which had been obtained from this solvent and dried in the air at ordinary temperature, only slowly changed to red. In one batch of crystals a number of the yellow were found after two and one-half days.

Ethyl Bromide.—Mercuric iodide is only slightly soluble in this solvent, much less so indeed than in ethyl alcohol. It dissolves to form a pale-yellow solution, which, when cooled down in a freezing-mixture, gave a small crop of yellow, irridescent, rhombic plates. Those that had been formed by sudden cooling were found to be very stable under the solvent, the change to red being complete only after standing twenty-four hours. The crystals obtained by allowing the solution to cool down gradually were found to alter more easily than those obtained by sudden cooling.

Isopropyl Bromide.—Mercuric iodide is only sparingly soluble in isopropyl bromide, giving a solution which in small amounts appears colorless. This is probably due to the small amount of the yellow compound in solution. From this solution, on sudden cooling, mercuric iodide separates out in yellow rhombs, also in numerous small fragmentary crystals. The whole mass slowly changed to red.

Isobutyl Bromide.—Mercuric iodide is only moderately soluble in this solvent. It gives a pink solution, from which, on sudden cooling, it gives a crystalline yellow precipitate, which is composed of very minute, fragmentary crystals. On gradual cooling the compound crystallizes out in the form of yellow needles, which slowly change to red.

Ethylidene Chloride.—Mercuric iodide is only slightly soluble in this solvent. The solution in small amounts is colorless. On sudden cooling at 18° C. the iodide crystallizes out in yellow plates, which quickly change to red.

Propyl Chloride.—This solvent dissolves mercuric iodide very sparingly, giving a pink solution. On cooling yellow crystals were obtained, which, under the microscope, were seen to consist of rhombs and rhombic plates.

Ethyl Cyanide.—Mercuric iodide dissolves very readily in ethyl cyanide, even more so than in ethyl alcohol. This solution is yellow, and on sudden cooling deposits yellow crystals, which were found to consist of rhombs and rhombic plates, and which were found to change to red with considerable rapidity. On gradual cooling the same form is obtained, only the crystals are larger.

Benzene Cyanide.—Mercuric iodide is only moderately soluble in benzene cyanide, but very little more so than in ethyl alcohol. It gives a deep-yellow solution, which, on sudden cooling, deposits yellow crystals, rhombs, rhombic plates and needles, which rapidly turn red. A solution on gradual cooling deposits yellow crystals, in which there are no needles, and in which the number of rhombs is greater; the solution in each case was obtained above the transition temperature of mercuric iodide.

Benzoic Acid.—Mercuric iodide dissolves in benzoic acid very rapidly at high temperatures. In fact, it proved one of the best solvents tried on this substance. A saturated solution was prepared at 180° C. The solution was yellow, and on gradual cooling, at 152° C., gave a large crop of crystals in the form of yellow irridescent plates.

Ethyl Acetate.—This solvent dissolves mercuric iodide very sparingly, much less readily than alcohol. It gives a yellow solution, from which crystals are deposited in the form of yellow irridescent plates.

Ethyl Propionate.—This solvent dissolves mercuric iodide fairly easily, and somewhat better than ethyl alcohol and ethyl acetate. The solution was found to have a light yellow color and to deposit crystals, even when warm, in the form of yellow needles.

Ethyl Butyrate.—Mercuric iodide was found to be very soluble in this solvent. The solution, made by saturating with the iodide at 150° C., was found to be yellow in color. On sudden cooling the iodide crystallized from this solution in large numbers of thin, prismatic crystals, yellow in color, and wanting in irridescence. On gradual cooling needle-shaped crystals of the yellow iodide were again obtained. Under the solvent these crystals were found to change to red very slowly, whereas the same crystals when exposed to air, out of contact with its solvent, altered very rapidly.

Ethyl Isobutyrate.—Mercuric iodide is soluble only to a moderate degree in this solvent, much less soluble than in ethyl butyrate, but soluble to about the same amount as in ethyl alcohol. It forms a pale-yellow solution in this solvent, and on sudden cooling crystallizes out in quantities of yellow needle-shaped crystals. On cooling gradually large numbers of perfect yellow rhombs are formed, especially at 100° C. These rhombs were found to alter in color more rapidly than the needle-shaped crystals. The yellow crystals changed more rapidly than those obtained from the butyrate, but less rapidly than those from ethyl propionate.

Methyl Salicylate (*Oil of Wintergreen*).—Mercuric iodide dissolves very readily in this solvent. At 117° C. a solution was prepared having a deep-yellow color. On sudden cooling yellow crystals are formed, which were found to consist mainly of the needle-shaped variety. These were found to be very stable. Some of the needle-shaped crystals were placed on a watch-glass and allowed to remain undisturbed for some time. The greater number of these were found to be unaltered after thirty-two hours, and some of them were unchanged after three days. On allowing the solution to cool gradually, yellow needles crystallize out while the solution is still warm, which are larger and finer than those obtained on sudden cooling; also about an equal number of rhombs and rhombic plates are obtained. The first portions that crystallize out consist almost entirely of needles, while the last portions consist almost entirely of rhombs and rhombic plates.

Phenyl Salicylate (*Salol*).—This substance dissolves mercuric iodide very sparingly at 145° C. The solution is yellow, and on sudden cooling the iodide crystallizes out in the form of small, yellow, needle-shaped crystals, which gradually change to red. On cooling slowly the iodide is obtained in the form of very long, thin, needle-shaped, yellow crystals, which very slowly change to red.

It will be seen from the above that solutions of mercuric iodide, with the exception of two, produced with alkyl halides, have a yellow color,[1] and that all solutions, without exception, deposit yellow crystals on cooling. Bancroft[2] has observed that water precipitates the yellow modification from a solution of mercuric iodide in methyl alcohol, and from this he drew the conclusion that on sudden precipitation the unstable form is the first to appear. It is also well known that mercuric iodide is yellow when first produced by double decomposition from aqueous solutions. It has been noted in the above that several solutions of mercuric iodide which deposit yellow crystals are themselves pink in color. Such solutions have been obtained with bromoform, ethylene bromide, propyl chloride, and isobutyl bromide. At first these were thought to be solutions of the red modification. On more careful examination, however, it was found that the pink color was not due to the red modification of the mercuric iodide, but to the formation of unstable alkyl iodides, which exhibit a pink coloration in the first stages of their decomposition. These unstable alkyl iodides are produced in such solutions by partial double decomposition with the mercuric iodide,

$$2C_3H_7Cl + HgI_2 = 2C_3H_7I + HgCl_2.$$

It will be observed that these pink solutions were only obtained with the alkyl halides as solvents. It would seem that the color of the red iodide of mercury is such that it ought to give red or pink solutions. The fact that only yellow solutions were obtained by dissolving the red iodide in these various solvents, and that the yellow modification alone crystallizes out of these solutions, would seem to indicate that in the act of solution, the transition-point of mercuric iodide (128° C.) is greatly lowered, for the production of these yellow solutions occurs with low- as well as with high-boiling solvents, the lowest boiling solvents tried being ethyl bromide 38°.4 C., propyl chloride 48° C., and acetone 56° C. In order to form a better idea of the change which occurs when the red mercuric iodide passes into solution, the following experiments were tried with amyl alcohol: A quantity of pure crystalline red iodide of mercury was put in a tube with amyl alcohol, the former being in excess of the amount required to form a saturated solution at the temperature of the experiment. The tube was then sealed and heated in a current of steam. Tubes of this character were heated for one, two, three, and eight hours. A yellow solution of mercuric iodide was obtained in each case, and invariably a thin film of the yellow variety, or a little mass of yellow crystals was found on top of the unchanged red iodide. Further, when such tubes were cooled, either gradually in the air or by plunging into cold water, crystallization always started on the top of the undissolved mass; that is, the small amount of the yellow variety already in the tube served as a nucleus for crystallization. After a time the solution above the unchanged red variety became filled with yellow crystals, and, on standing, these also changed to red, the change taking place in every instance from the surface of contact with the red up, indicating that the yellow changes quickest in contact with the red modification. In such tubes the difference between the two varieties of the compound is so striking and the line of demarcation between the two so sharp as to make this a beautiful method for exhibiting these two varieties of the iodide. It would seem, therefore, that when amyl alcohol is brought together with the red modification in excess, a certain number of molecules of the red modification of the iodide change to yellow and at once pass into solution. When equilibrium is reached, however, there are as many molecules passing out of the solution as are passing in, and these are also of the yellow variety. That such is the case is seen from the small mass or film of yellow crystals, which is invariably formed by heating the solution of mercuric iodide in contact with an excess of the red variety of this compound. That the red variety is not entirely changed to yellow by first passing into the solution and then crystallizing out is probably due to the fact that, by contact with a certain amount of the red variety remaining in the tube, the yellow is rapidly changed to red as it separates from the solution. Hence we would have the solvent constantly changing the red modification to yellow and dissolving it and again precipitating it. This last, however, would tend to pass back to the red as soon as removed from the solution. The idea that red mercuric iodide itself is insoluble in these various solvents would seem to derive support from the insolubility of allotropic modifications of other substances. As is well known, red phosphorus is insoluble in most solvents, and from solutions in the few solvents in which it is soluble, only yellow phosphorus can be obtained. Then again, the remarkable insolubility of the several forms of carbon, the transition temperature of which is probably very high, is interesting and suggestive in view of these considerations. In dealing with the facts set forth in the above, it is almost impossible to avoid the much-discussed question : *What is in the solution ?* In the case of sulphur two entirely different answers have been given to this question. As the result of his investigations Deville[1] came to the conclusion that there was a distinct difference in solutions of sulphur. This, however, has been denied by others, among them Ostwald. In the latter's "Outlines of General Chemistry," English Translation, p. 191, we find the following bearing on this point : "When allotropic solids are brought into the liquid or gaseous state not a trace of difference between them is left. The vapor of red phosphorus is identical with the vapor of yellow phosphorus, and a solution of rhombic sulphur in carbon disulphide is in no respect different from a solution of similar composition made from monosymmetric sulphur. Conversely, from the same solution, *e. g.*, one of nickel sulphate supersaturated by cooling, any one of the different forms of the salt may be obtained by the introduction of a fragment of the corresponding crystal. The so-called physical isomerism thus occurs exclusively in connection with the solid substance, and disappears whenever the latter assumes another state of aggregation."

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[1] In an article on "The Color Relations of Atoms, Ions, and Molecules," M. Cary Lea, Chem. News, 73, 260, describes a solution of mercuric iodide in alcohol as absolutely colorless. He evidently failed to compare the color of this solution with that of the pure solvent.

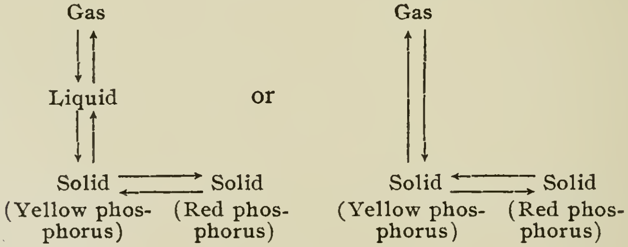
[2] Jour. Phys. Chem., 1, 142 (1896).

Unfortunately in spite of their clearness, these considerations do not afford a sufficient explanation of the changes occurring in the solution of mercuric iodide. It is certain that one characteristic property of the yellow variety of mercuric iodide is still preserved when it goes into solution. This is its

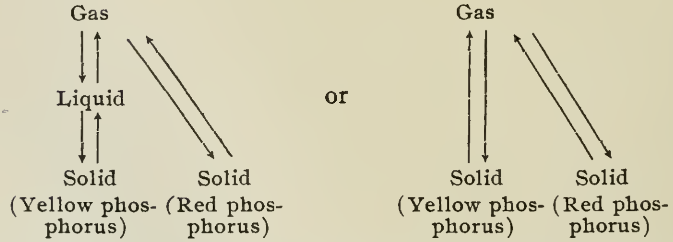
[1] Compt. rend., 26, 117 (1848).

yellow color. While this solution can be made by starting with either the red or the yellow modification, the converse of this is not true. A crop of red crystals is not obtained by the introduction of a red crystal into the solution, but crystals of the yellow variety only. This has been shown in experiments with amyl alcohol.

The conclusion, therefore, seems logical that solutions of mercuric iodide really contain the yellow modification of this compound and not simply molecules of HgI_2, which may arrange themselves in the yellow or red modification of this compound according to the nature of the crystal form which is first presented to them. In the case of phosphorus, for example, it is quite probable that nothing is known of red phosphorus as a gas or in solution, for the reason that the conditions necessary to change it into the gaseous state or to cause it to pass into solution, probably first change it into the yellow variety.[1] These changes might be represented in this way :



and not



So, in the same way, on vaporization and solution and the reverse, the changes occurring in the red iodide of mercury might be represented thus :

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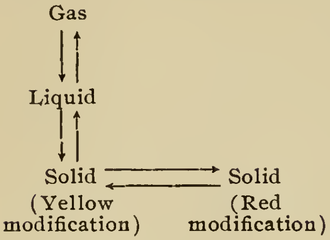
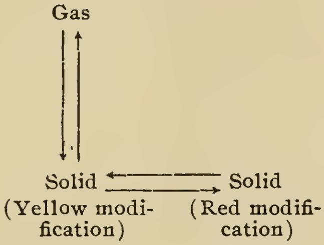
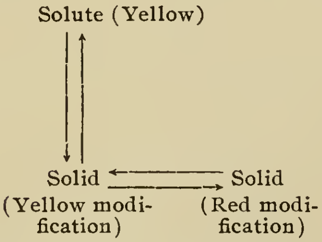
[1] Comey's Dictionary of Chemical Solubilities, p. 317 (1896).



Or in the event of sublimation, thus :



Or by solution, thus :



It is interesting to note, in this connection, that mercuric iodide, both as a gas and solute, is yellow in color. It would seem, therefore, that the yellow modification of mercuric iodide (solid) is identical with that which exists in its solutions, or is perhaps a polymer of the same.

Since this article went to press our attention has been called to some recent work by Gernez[1] on the vaporization of mercuric iodide in vacuo. He has shown that the vapor given off at all temperatures by the yellow variety of this compound deposits yellow orthorhombic crystals, no matter what may be the temperature of the cooler surface on which the deposition occurs. The yellow crystals are also obtained from the vapor

[1] Compt. rend. (1899), 128, 1516, 1519.

emitted by the red variety when vaporized at any temperature from 25° C. up to the transition temperature. If, however, the cool surface is slightly rubbed with the red crystals, the form deposited is also red. It is believed that these results of Gernez present nothing at variance with the views advanced in the above.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KY., Sept., 1899.

Contribution from the Kent Chemical Laboratory of the Yale University.

THE ETHERS OF ISONITROSOGUIACOL IN THEIR RELATION TO THE SPACE ISOMERISM OF NITROGEN.

BY JOHN L. BRIDGE AND WM. CONGER MORGAN.

When the presence of isomerism in the quinoneoximes was first noted by one of us[1], and the phenomenon exhibited by the two isomeric ethers then described was shown by Kehrmann[2] to be due to no structural differences, but to necessitate the assumption of a spatial arrangement about the nitrogen atom, according to the theory of Hantzsch and Werner, the plan was adopted of studying the various substituted quinoneoximes, by means of their acyl and alkyl ethers, with reference to this phenomenon. Accordingly we have investigated the toluquinoneoximes[3], both ortho and meta, producing them by the action of nitrous acid on the cresol as well as by hydroxylamine on toluquinone, and found that, whereas there is abundant evidence for the existence of stereoisomeric bodies in the metaoxime ethers, in the derivatives of the orthooxime, all such indication is wanting. The significance of this observation is furthermore increased by the fact that all oximes, in which isomerism has been reported, may be considered as derivatives of metasubstituted quinones, and it seemed not improbable, therefore, that these observations might be formulated into a general rule regarding the appearence of isomerism in the quinoneoximes.

In the course of his investigation of the properties and reactions of isonitrosoguiacol, among other derivatives, Pfob[1] made the methyl and acetyl ethers, but did not announce the observation of any cases of isomerism. Isonitrosoguiacol may be considered as the metamethoxyquinoneoxime, hence this metasubstituted quinoneoxime presented conditions differing widely from the other members of the same series above mentioned. Moreover, because of its close relationship to toluquinonemetaoxime, from which it differs only by the interposition of an oxygen atom between the ring and the methyl group, it seemed possible that isomeric modifications of the ethers might exist, which had been overlooked by the former investigator. When, furthermore, Rupe[2] made no mention of such appearence in his research on isonitrosoguiacol, it seemed advisable to undertake anew the investigation of this body with the special purpose of discovering such isomerism, if possible, and to couple with it an investigation of the orthomethoxyquinoneoxime or isonitroso derivative of the monomethyl ether of resorcin, in order by this means to be able to parallel in these closely analogous bodies the experiments with the ortho- and metacresols.

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[1] Ann. Chem. (Liebig), **277**, 79.

[2] *Ibid.*, **279**, 27.

[3] This JOURNAL, **20**, 761; **22**, 402.

With this idea, the work of Pfob and Rupe was carefully repeated, so far as it pertained to the question in hand, but, aside from minor differences, our results served only to corroborate the testimony of these investigators. New derivatives, to be described later, were prepared in the hope that these bodies might show some variations leading to the discovery of isomeric modifications, but each appeared to be entirely homogeneous and no evidence for isomerism could be found. These results are of course only negative and do not disprove the existence of space isomers in the same bodies, yet the same methods, which gave very positive evidence of their presence in other quinoneoxime ethers, were used to detect them in this instance.

Aside from the difficulty of obtaining pure monomethyl ether of resorcin in any considerable quantity, because of poor synthetical processes and inefficient methods of separation, inasmuch as preliminary experiments pointed to a multiplicity of products in the reaction with nitrous acid such as Kietaibl[1] found with the monoethyl ether, it was thought inadvisable in the light of the results obtained with the meta body, to continue the work on the ethers of orthomethoxyquinoneoxime. Work along the general line will be continued, and the results of experimentation with mononitrosoresorcin will soon appear.

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[1] Monatsh. Chem., 18, 467.

[2] Ber. d. chem. Ges., 30, 2444.

EXPERIMENTAL PART.

Isonitrosoguiacol and Salts.

The isonitrosoguiacol used in the investigation was prepared both by the method of Pfob, working with nascent nitrous acid in alcoholic solution, and also by the general method for the formation of the sodium salts of isonitroso bodies suggested by Walker.[2] To a concentrated alcoholic solution of sodium alcoholate, guiacol is added in sufficient quantity to form the sodium salt by the resulting metathesis, then, to this solution of sodium guiacol, slightly more than the theoretical quantity of amyl nitrite is added and, after thorough mixing, the liquid is allowed to stand over sulphuric acid for twenty-four hours, when the bright olive-green crystalline sodium salt of isonitrosoguiacol separates. After washing thoroughly with ether, pulverizing and rewashing, the salt may be used directly for the preparation of derivatives, or, if further purification is desirable, it may be dissolved in water, acidified with hydrochloric acid, and the filtered and dried product dissolved in ether and shaken with animal charcoal, when, upon evaporation, the pure isonitrosoguiacol crystallizes. Of the above methods of preparation the latter is much to be preferred, although Rupe mentions it unfavorably because of poor yields and impure products. He advocates the use of ethyl nitrite in a closed tube; but on trial we were unable to obtain the quantitative yields which he reports and the seventy per cent yield which the amyl nitrite gives, makes this method quite equal, in efficiency as well as purity of reaction-product, to the other more tedious process.

The silver salt, formed from the sodium salt by treating the aqueous solution with a slight excess of silver nitrate, comes down as a brown gelatinous precipitate, which becomes crystalline on gently warming, or may be obtained in crystalline form at once by heating the separate solutions to 50° C. before mixing. It is a very unstable salt, the dry product decomposing with a very gentle heating.

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[1] Monatsh. Chem., **19**, 536.

[2] Ber. d. chem. Ges., **17**, 399.

Isonitrosoguiacol Benzoyl Ether.

The sodium salt formed as above was dissolved in as little water as possible and four or five times its volume of alcohol added. This solution was thoroughly shaken with a slight excess of benzoyl chloride, added drop by drop. The reaction is immediate and the ether soon begins to come out of the solution in almost pure condition. Recrystallized from alcohol, it separates in straw-colored, branching crystals, which melt sharply at 188° C. when "dipped" for ten seconds. Heated gradually from normal temperatures, it begins to decompose at 175° C. and liquefies at 185°–188° C., the temperature depending on the rapidity with which heat is applied.

Fractional crystallization from alcohol or other solvents did not essentially change the melting-point, nor were any different phenomena observed when the isonitrosoguiacol was made by the acid reaction. This ether dissolved readily in chloroform and glacial acetic acid, much less in benzene and ligroin, and is practically insoluble in ether and carbon disulphide. On analysis:

0.1100 gram of the substance, dried over H_2SO_4, gave 0.2632 gram CO_2, and 0.0428 gram H_2O.

0.1205 gram of the substance gave 5.45 cc. N at 15° C. and 772 mm. pressure.

	Calculated for $C_{14}H_{11}O_4N$.	Found.
C	65.34	65.26
H	4.31	4.32
N	5.46	5.38

Isonitrosoguiacol Benzoyl Ether Dibromide.

Three grams of the benzoyl ether were dissolved in 25 cc. of chloroform and 2 grams of bromine were added, the mixture being kept cool by running water. The solution was allowed to stand for from one to two hours and then to evaporate spontaneously. The dibromide is left behind as a light-brown substance. Attempts to crystallize from glacial acetic acid proved unsatisfactory, since the boiling solvent caused a decomposition of the ether; nor did a solution in fuming nitric acid, precipitated by water, give a pure white product. The best results were obtained by washing with warm dilute alcohol when the product becomes yellowish-white, and melts at 153°–154° C., browning considerably above 140° C. An analysis of the substance purified in this manner shows a low percentage of bromine.

0.1052 gram of the substance, dried over H_2SO_4, gave 0.1547 gram CO_2, and 0.0284 gram H_2O.

0.0509 gram of the substance gave 0.0449 gram AgBr.

	Calculated for $C_{14}H_{11}O_4NBr_2$.	Found.
C	40.29	40.10
H	2.66	3.00
Br	38.34	37.52

Monobromisonitrosoguiacol Benzoyl Ether.

By boiling the white dibromide with 60 per cent alcohol for three-quarters of an hour, the halogen acid and a bright-yellow monobromine compound are formed. This ether crystallizes from boiling alcohol in the characteristic prismatic form of such bodies and melts with decomposition at 178° C. Repeated recrystallizations did not change this melting-point and no indication was noted suggesting the possibility of a mixture. On analysis:

0.1317 gram of the substance, dried over H_2SO_4, gave 0.2410 gram CO_2, and 0.0368 gram H_2O.

0.2101 gram of the substance gave 0.1172 gram AgBr.

	Calculated for $C_{14}H_{10}O_4NBr$.	Found.
C	49.99	49.91
H	3.00	3.11
Br	23.79	23.75

JUNE, 1899.

TEXAS PETROLEUM.

By F. C. Thiele.

It has long been known that mineral oil existed in the State of Texas, but only of late has this discovery been utilized. About three years ago oil was discovered in the town of Corsicana, and further researches proved that Corsicana was literally built on a vast oil-pool. About 400 wells are in operation at present. A big refinery was built to dispose of the natural product, and Corsicana is a flourishing town to-day. All this was accomplished in the short space of a couple of years through an accidental discovery.

The Corsicana oil, as it comes from the wells, resembles in its appearance the Lima-Ohio oil, without having, however, the disagreeable odor, so characteristic of the oil found in the Ohio-Indiana district. An analysis made by the author shows the Corsicana oil to be composed as follows :

Crude Oil—Specific Gravity = 0.8296.

	Per cent.	Specific gravity.
Naphtha	10.8	0.710
Kerosene	54.5	0.796
Residue	34.7	0.905
	100.0	

A more elaborate analysis made by Mr. E. H. Ernshaw shows the following composition of the Corsicana oil.

Oil very dark-brown and opaque, but thin and fluid at 60° F. Specific gravity at 60° F. = 0.8292.

	Temp., °F	Percentage by volume.	Percentage by weight.	Specific gravity at 60° F.	Color, etc.
A	130–200	2.80	2.24	0.6653	Colorless
B	200–250	5.10	4.31	0.7017	
C	250–300	7.60	6.69	0.7302	
D	300–350	8.20	7.44	0.7527	
E	350–400	9.40	8.75	0.7718	
F	400–450	7.40	7.07	0.7920	
G	450–500	8.30	8.09	0.8088	
H	500–550	6.45	6.43	0.8260	Very faint yellow
I	550–600	7.75	7.85	0.8404	" " "

	Temp., °F.	Percentage by volume.	Percentage by weight.	Specific gravity at 60° F.	Color, etc.
J	600–650	14.95	15.43	0.8555	Yellow
K	650–665	17.25	18.07	0.8687	Deep reddish-yellow
L	over 650	1.30	1.41	0.8972	Deep red—solid
M	over 650	1.40	1.63	0.9699	Dark red-brown—solid
	Residue	....	2.63	.....	
	Total	97.90	98.04		

The above analysis shows the Corsicana oil to be closely related to Pennsylvania oil, especially that of the Washington district, but it contains, according to my researches, a certain amount of asphaltum or bodies very similar to it. The presence of asphaltum compounds in crude oils can easily be demonstrated by the addition of tin tetrachloride, $SnCl_4$, to a sample of the oil in question. If a black precipitate is formed on the addition of the reagent, asphaltum or similar compounds are present in the oil. I found this reaction to be of value for oils which are subjected to distillation, as oils containing asphaltum should be distilled with great care and a very gradual rise of temperature, so as not to get too large an amount of the terpene-like decomposition-products of the asphaltum in the distillates. The presence of these bodies, which resemble aromatic hydrocarbons, tend to color the oil yellow, and even a very effective acid treatment does not seem to improve the oil much in color. This behavior of the distillates resembles the one which oils show when they have been subjected to overheating, as in the case of certain desulphurizing processes, proposed for the purification of strongly sulphur-bearing oils, such as Lima, Canadian, and others.

It was soon found, after the Corsicana oil field was discovered, that oil existed in other places in Texas, and borings for it were rapidly made in a number of places. It soon developed that a well-defined oil stratum existed, which, following the Trinity river to Nacogdoches, and turning here and following the Sabine River, flowed out into the Gulf of Mexico at Sabine Pass, covering the water at times with a black greasy substance over quite a large area.

The oil found at Nacogdoches is very heavy, its specific gravity being 0.915. Its color is black, and it is strongly impregnated with sulphuretted hydrogen. It occurs in shallow wells not over 90 feet deep, and very likely belongs to the class of oils which are described in the literature as maltha.

From Nacogdoches, going south, the oil makes its next appearance at Rockland, the terminus of the Rockland, Sabine Pass Railroad. It is asserted that the oil exists here in large quantities, but no researches regarding its properties have been made. Saratoga, south of Rockland, is the next place where oil deposits are found, and experimental boring has been going on here for some time. The oil found here is still heavier than the Nacogdoches oil, having a specific gravity of 0.955. It is a black oil rich in asphaltum.

Fourteen miles south of Saratoga is the watering-place of Sour Lake, where a large oil deposit occurs. The soil at Sour Lake is undoubtedly of volcanic character, judging by the large variety of waters found here, and the general condition of the territory.

The crude petroleum found at Sour Lake occurs at a depth of 250 feet in the alluvial formation, and is what is termed a "surface oil." Its specific gravity at 63°.5 F. is 0.963, which is the highest specific gravity observed with any crude oil found on the western hemisphere. A fractional distillation of the oil shows the following constituents:

Fraction.	Temperature, °F.	Percentage by volume.	Specific gravity.	Color, etc.
1	....	....	....	
2	212–266	0.07	....	Yellow
3	266–320	0.03	....	"
4	320–392	1.59	0.684	"
5	392–572	19.49	0.840	" blue fluorescence
6	....	....	....	
7	572–641	5.15	0.782	Dark-yellow
Residue		71.11	0.978	Black
Total		97.44		

The oil contained 20 per cent asphaltum.

The analysis was carried out according to the directions laid down by R. Kissling during his investigations of crude oils of different origin.

The above analysis indicates that the greater part of the oil is composed of hydrocarbons excellently suited for lubricating purposes, and the last fraction has a viscosity of 19° (Engler apparatus), a figure which exceeds that of the heaviest Russian products. Tests which were made on the large scale showed the presence of aromatic hydrocarbons, such as pseudocumene and others, and according to its behavior the crude oil may be called a true representative on American soil, of the oil found at Wietze-Steinförde, Germany, which was pronounced by Prof. Engler one of the most valuable sources of high-grade lubricating oils, if it could be freed of its asphaltum by proper refining and treatment. Solid paraffin has not been found in the crude oil, nor in any of the refined products, and it is doubtful whether any is present.

As to the origin of the oil, the presence of aromatic hydrocarbons and the absence of solid paraffin would indicate a vegetable origin, but, on the other hand, nitrogen products and a large amount of sulphur have been found in the oil, and these facts favor the view that it is of animal origin.

I cite here a test which I made to further advance the knowledge of this interesting oil. Some of the oil was dissolved in benzene, C_6H_6, which dissolved it with the separation of some water. The latter was removed and alcohol of 85 per cent added until no further precipitation occurred. The whole was well shaken, and after standing for some time the supernatant clear liquid was removed from the black resinous mass formed on the bottom of the vessel. The clear liquid was evaporated on a water-bath at a temperature of 80° C. A very viscous oil remained behind, which, when heated to 120° C., gave a very decided odor of musk.

The black resinous mass, dried at 120° C. for several hours, presented, after cooling, the general properties of "goudron," but had an odor which could not be distinguished from rancid stearin. This distinguishing feature recalls some experiments which were published in the "Chemiker Zeitung" several years ago on the distillation of so-called "stearin-pitch." Products were obtained which resembled in every respect the distillates obtained from mineral oils. As stearin is undoubtedly of animal origin, the above discovery may furnish further evidence of the correctness of the theory of Höfer and Engler.

It has often been asserted that the water which comes up with the crude oil when the latter is pumped out of the well does not contain any sulphates or merely traces of them. C. Ochsenius especially expressed this opinion very strongly and tried to prove that such was the case in every instance. The conditions are, however, different in Sour Lake. As I have stated already the character of the territory there is undoubtedly volcanic, and numerous water wells occur there which are very strong in sulphates, especially alumina, and contain in many instances large amounts of free sulphuric acid. The water coming out of the ground carries with it considerable oil, which floats on it as a thick black tar. The oil wells which were sunk artificially contain water, which is strong in chloride of sodium, but still contains a considerable amount of sulphates. Whether the occurrence of this large amount of sulphates and free sulphuric acid is related to the genesis of the oil or not is an open question, but as the opinions are still divided on this subject I deemed it necessary to mention the facts as they are presented by nature.

NOTE.

Solid Hydrogen.

In a recent number of the *Chemical News*,[1] Dewar describes the method by which he solidified hydrogen. He at first attempted to secure it by suspending a Dewar vacuum tube, partly filled with liquid hydrogen, inside of a larger vacuum tube containing the liquid hydrogen, and evaporating the liquid under diminished pressure. All the experiments carried out in this way failed, probably on account of supercooling of the liquid. By working under different conditions, however, he succeeded in obtaining the solid material and showed that it has no metallic character, but must be classed among the non-metallic elements.

The apparatus which he used was as follows: "A flask, *C*, of about a liter capacity, to which a long glass tube bent twice at right angles was sealed, as shown in the illustration, and to which a small mercury manometer can be sealed, was filled with pure dry hydrogen and sealed off. The lower portion, *AB*, of this tube was calibrated. It was surrounded with liquid hydrogen placed in a vacuum vessel arranged for exhaustion. As soon as the pressure got well reduced below that of the atmosphere, perfectly clear liquid hydrogen began to collect in the tube AB, and could be observed accumulating until, at about 30 to 40 mm. pressure, the liquid hydrogen surrounding the outside of the tube suddenly passed into a solid, white, foam-like mass, almost filling the whole space. As it was not possible to see the condition of the hydrogen in the interior of the tube AB, where it was covered with a large quantity of this solid, the whole apparatus was turned upside-down in order to see whether any liquid would run down AB into the flask C. Liquid did not flow down the tube, so the liquid hydrogen, with which the tube was partly filled, must have solidified. By placing a strong light on the side of the vacuum test-tube opposite the eye, and maintaining the exhaustion to about 25 mm., gradually the solid became less

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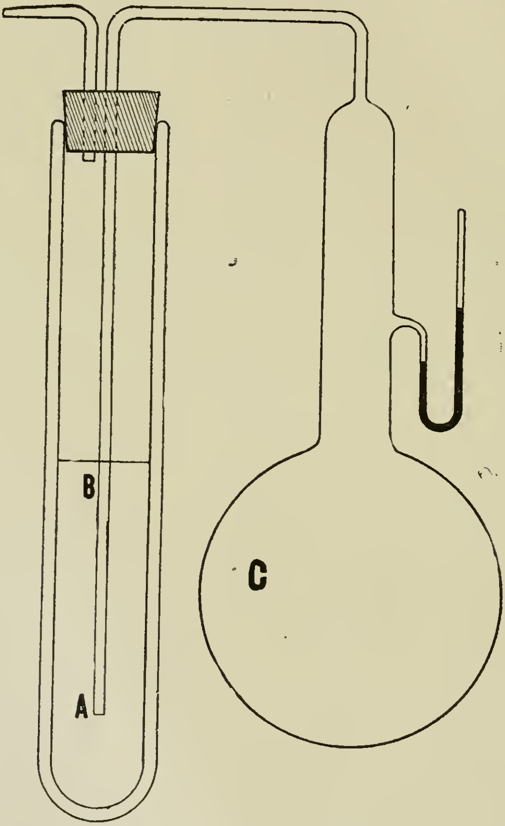
[1] Chem. News, 80, 132.



opaque, and the material in AB was seen to be a transparent ice in the lower part, but the surface looked frothy." The melting-point of hydrogen must be about 16° or 17° absolute, and the limit of temperature which can be obtained by the evaporation of solid hydrogen is from 14° to 15° absolute.

J. E. G.

REVIEWS.

INORGANIC CHEMICAL PREPARATIONS. BY FELIX LENGFELD, Assistant Professor of Inorganic Chemistry in the University of Chicago. New York: Macmillan Co. 1899. 55 pp.

This little manual indicates the spread of the newly-revived custom of making inorganic preparations an essential part of the laboratory work. There is nothing new in the idea. In the Göttingen laboratory and in other German laboratories during Wöhler's lifetime, inorganic preparations were made by every student, but since then, in nearly all laboratories, the number required has been gradually reduced to the few elementary gases and simple salts now generally required.

Hugo Erdmann's manual, published at Halle in 1893, was the first attempt to revive the custom. Confining ourselves to this country, Johns Hopkins adopted a privately printed manual in 1894; Vulté and Neustadt, of Columbia, published one in 1895; and F. H. Thorp, of the Massachusetts Institute of Technology, another in 1896. As to the present book, Professor Lengfeld has made an excellent selection; he expects the student in each case to study the original article to which he gives the reference. Thus his book is especially addressed to advanced students, though it would be available for others with an instructor's help. It can be cordially recommended.

E. R.

THE CHEMISTRY OF SOILS AND FERTILIZERS. BY HARRY SNYDER, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Agricultural Experiment Station. Easton, Pa.: Chemical Publishing Co. 1899. 277 pages. Price, $1.50.

In the present age of competition, when every method of artificial production is being pushed to its limit, as far as the yield is concerned, the skill of the scientist has been called to aid this development. For various reasons the farmer has, of all classes, probably availed himself least of this aid and is still, in many cases, carrying on his work by methods which have been shown to be more injurious than beneficial. It is questionable whether the efforts of the Agricultural Experiment Station to overcome these difficulties and to aid the farmer have met with the desired results, on account of the unintelligible form in which the information is often supplied to him.

Within the last few years the farmers in many sections have realized that much material is being lost through their lack of knowledge of the principles of the changes taking place in the soil, and the scientific application of fertilizers. By the aid of farmers' conferences and short courses of instruction by trained experts on well-arranged experimental grounds, many farmers have learned to carry on their work in a scientific manner and to supply the waste by the right material in the right amount. The author of this book uses it as a guide in a course given to men who expect to become farmers. If all the young men who expect to follow this profession would take such a course of instruction, it would not be many years before the cultivation of the soil would be carried on in as scientific and business-like a manner as it is in many parts of Europe, where land is dear, and the most improved methods must be used to produce financial success. An idea of the general ground covered by this book can be seen from the headings of the chapters. The subject is treated under the following heads: The classification of soils, physical and chemical properties; nitrogen, its uses, methods of formation, occurrence and fixation; various classes of manures and fertilizers; and requirements and rotation of crops. The book is written in such a way as to be intelligible even to one who has had no scientific training, and it would be well for every farmer to read it, as it might stimulate him to study the problems more thoroughly, and put in practice many of the suggestions.

J. E. G.

PRACTICAL METHODS FOR DETERMINING MOLECULAR WEIGHTS. By HENRY BILTZ, Privatdocent at the University of Greifswald. Translated (with the author's sanction) by HARRY C. JONES, Associate in Physical Chemistry in Johns Hopkins University, and STEPHEN H. KING, M.D., Harvard University. Easton, Pa.: Chemical Publishing Co. 1899. 230 pages. Price, $2.00.

The German edition of this work was reviewed in this JOURNAL (**20**, 434) and its character fully described. In the translation some additions and changes, suggested by the author, have been made, and the work has been brought up to date. Its value as a text-book and laboratory guide can be best described by an extract from the translators' preface. "It can be fairly claimed that there is no book in English, and probably not in any other language, which deals with the problem of molecular weight determinations as satisfactorily as this recent publication by Biltz. We believe that the book will not only be useful in the laboratory, but, on account of its method of treatment, will also prove to be of service as a book of reference to the literature of molecular weight determinations."

J. E. G.

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